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(54) Title: METAL CHELATES

(57) Abstract: A photovoltaic device which uses a metal chelate as the photovoltaic element.

WO 2004/008554 A2

- 1 -

Metal Chelates

The present invention relates to photovoltaic devices and elements useful in such devices.

5 Photovoltaic devices, i.e. solar cells, are capable of converting solar radiation into useable electrical energy. The energy conversion occurs as a result of what is well known in the solar cell field as the photovoltaic effect. Solar radiation impinging on a solar cell and absorbed by an active region generates electrons and holes. The
10 electrons and holes are separated by a built-in electric field, for example a rectifying junction, in the solar cell. This separation of electrons and holes results in the generation of an electrical current as explained below. For example, a built-in electric field can be generated in a solar cell by an active semiconductor layer with regions of P-type, intrinsic and N-type hydrogenated amorphous silicon. A built-in electric field
15 can also be generated in a solar cell by, for example, a Schottky barrier. The electrons generated at the metal (Schottky barrier) semiconductor body junction flow towards the semiconductor body.

A typical simple photovoltaic solar cell comprises an electrically conductive substrate
20 layer; a semiconductor body deposited upon said substrate layer and a transparent conductive layer over at least a portion of said semiconductor body for facilitating collection of electrical current produced by the photovoltaic cell.

The electrons generated in the intrinsic region, by absorption of solar radiation of the
25 appropriate bandgap, produce electron-hole pairs. The separation of the electron-hole pairs with the electrons flowing toward the region of N-type conductivity, and the holes flowing toward the region of P-type conductivity, creates the photovoltage and photocurrent of the cell.

30 The photocurrent output of a solar cell is maximized by increasing the total number of photons of differing energy and wavelength which are absorbed by the

- 2 -

semiconductor material. The solar spectrum roughly spans the region of wavelengths from about 300 nanometers to about 2200 nanometers, which corresponds to from about 4.2 eV to about 0.59 eV, respectively. The portion of the solar spectrum which is absorbed by the solar cell is determined by the size of the bandgap energy of the semiconductor material. In the past, solar cells were fabricated from single crystal materials such as gallium arsenide, which has a bandgap energy of about 1.45 eV, or crystalline silicon, C-Si, which has a bandgap energy of about 1.1 eV. Solar radiation having an energy less than the bandgap energy is not absorbed by the semiconductor material, and thus does not contribute to the generation of the photocurrent output of the cell.

Semiconductor materials such as GaAs and C-Si have been utilized together in solar cells to increase the overall conversion of solar energy into electrical energy. However, problems are encountered when different semiconductor materials are used in the same solar cell. One solution to the problem of fabricating a solar cell structure with different semiconductor materials was to use filters to reflect light of the appropriate wavelength onto a solar cell of the first material and transmit the non-absorbed light to a cell of the second semiconductor material. A second solution used semiconductor materials of differing bandgaps which could be epitaxially grown on one another, such as aluminum gallium arsenide, gallium arsenide, and gallium phosphide structures. Both these systems have been loosely called tandem junction solar cells. A third alternative was to stack individual solar cells of differing bandgap energies and connect the cells in series. These three alternatives are either cumbersome, expensive and/or bulky. A description of photovoltaic cells and their operation is disclosed in a paper by Jean-Michel Nunzi in C.R.Physique 3 (2002) 523-542.

We have found that a photovoltaic device can be made using metal chelates such as a rare earth or non rare earth metal chelate or a mixture of rare earth metal chelates as the photovoltaic element in place of the prior art semi conductors.

Rare earth chelates are known which fluoresce in ultra violet radiation and A. P. Sinha (Spectroscopy of Inorganic Chemistry Vol. 2 Academic Press 1971) describes several classes of rare earth chelates with various monodentate and bidentate ligands.

5

Group III A metals and lanthanides and actinides with aromatic complexing agents have been described by G. Kallistratos (Chimica Chronika, New Series, 11, 249-266 (1982)). This reference specifically discloses the Eu(III), Tb(III), U(III) and U(IV) complexes of diphenyl-phosponamidotriphenyl-phosphoran.

10

EP 0556005A and 0744451A also disclose fluorescent chelates of transition or lanthanide or actinide metals.

Patent application WO98/58037 describes a range of lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices using rare earth chelates.

15

Hitherto such rare earth metal chelates have not been used in photovoltaic devices.

20

According to the invention there is provided a photovoltaic device comprising a metal chelate as the photovoltaic element.

The invention also provides a photovoltaic device which comprises sequentially (i) a first electrode comprising a metal, (ii) the photovoltaic element and (iii) a second electrode in which the photovoltaic element comprises a metal chelate.

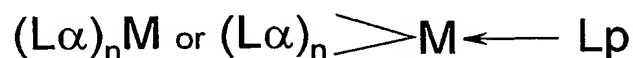
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By photovoltaic element is meant a compound which will generate electrons and holes when exposed to light.

30

The metal chelates can absorb light of a specific wavelength or wavelengths depending on the metal and ligands used and, as the photocurrent output of a solar cell is maximized by increasing the total number of photons of differing energy and wavelength which are absorbed by the semiconductor material, by having a plurality of layers of different metal chelates which absorb light at different wavelengths, a wide range of the visible spectrum can be used. Metal chelates can also absorb light in the infra-red, ultra-violet or shorter wavelengths so improving the utilisation of sunlight and increasing the power achievable by a solar cell. Alternatively there can be several layers of metal chelates which absorb light in different parts of the spectrum.

The preferred metal chelates useful in the present invention have the formula



15

where $L\alpha$ and L_p are organic ligands, M is a metal and n is the valence state of the metal M and in which the ligands $L\alpha$ are the same or different.

There can be a plurality of ligands L_p which can be the same or different.

20

For example $(L_1)(L_2)(L_3)(L_{..})M (L_p)$ where M is a metal e.g. rare earth, transition metal, lanthanide or an actinide and $(L_1)(L_2)(L_3)(L_{..})$ are the same or different organic complexes and (L_p) is a neutral ligand. The total charge of the ligands $(L_1)(L_2)(L_3)(L_{..})$ is equal to the valence state of the metal M . Where there are 3 groups $L\alpha$ which corresponds to the III valence state of M the complex has the formula $(L_1)(L_2)(L_3)M (L_p)$ and the different groups $(L_1)(L_2)(L_3)$ may be the same or different.

25

Lp can be monodentate, bidentate or polydentate and there can be one or more ligands Lp.

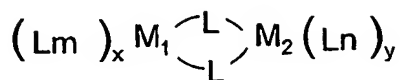
Preferably M is a metal ion having an unfilled inner shell and the preferred metals are selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Gd(III) U(III), Tm(III), Ce (III), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III) and more preferably Eu(III), Tb(III), Dy(III), Gd (III).

Further compounds which can be used in the present invention are of general formula $(L\alpha)_n M_1 M_2$ where M_1 is the same as M above, M_2 is a non rare earth metal, $L\alpha$ is as above and n is the combined valence state of M_1 and M_2 . The complex can also comprise one or more neutral ligands Lp so the complex has the general formula $(L\alpha)_n M_1 M_2 (Lp)$, where Lp is as above. The metal M_2 can be any metal which is not a rare earth, transition metal, lanthanide or an actinide; examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

For example $(L_1)(L_2)(L_3)(L_{\dots})M (Lp)$ where M is a rare earth, transition metal, lanthanide or an actinide and $(L_1)(L_2)(L_3)(L_{\dots})$ and (Lp) are the same or different organic complexes.

Further organometallic complexes which can be used in the present invention are binuclear, trinuclear and polynuclear organometallic complexes e.g. of formula $(Lm)_x M_1 \leftarrow M_2 (Ln)_y$ e.g.

- 6 -

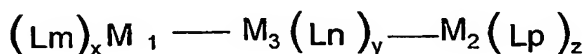


where L is a bridging ligand and where M_1 is a rare earth metal and M_2 is M_1 or a non rare earth metal, Lm and Ln are the same or different organic ligands La as defined above, x is the valence state of M_1 and y is the valence state of M_2 .

In these complexes there can be a metal to metal bond or there can be one or more bridging ligands between M_1 and M_2 and the groups Lm and Ln can be the same or different.

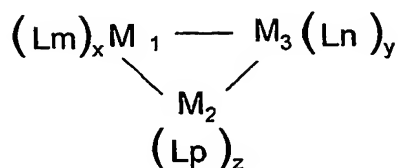
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By trinuclear is meant there are three rare earth metals joined by a metal to metal bond i.e. of formula



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or

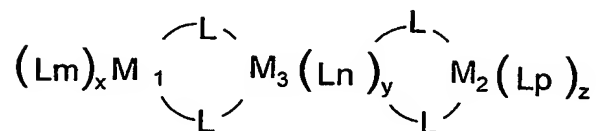


20 where M_1 , M_2 and M_3 are the same or different rare earth metals and Lm, Ln and Lp are organic ligands, La and x is the valence state of M_1 , y is the valence state of M_2 and z is the valence state of M_3 . Lp can be the same as Lm and Ln or different.

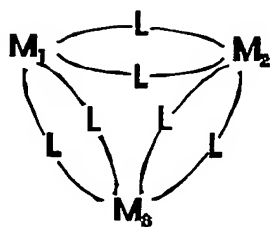
25 The rare earth metals and the non rare earth metals can be joined together by a metal to metal bond and/or via an intermediate bridging atom, ligand or molecular group.

- 7 -

For example the metals can be linked by bridging ligands e.g.

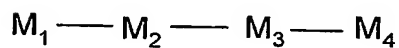


5 or



where L is a bridging ligand

10 By polynuclear is meant there are more than three metals joined by metal to metal bonds and/or via intermediate ligands

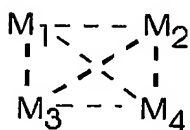


or

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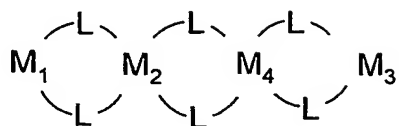


or



20 or

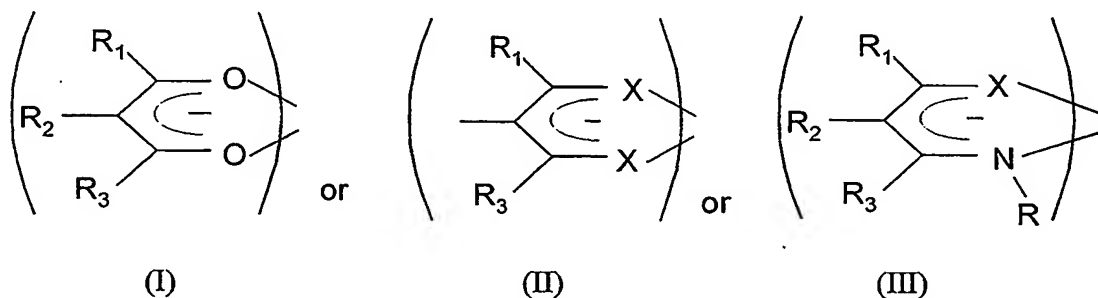
- 8 -



where M_1 , M_2 , M_3 and M_4 are rare earth metals and L is a bridging ligand.

- The metal M_2 can be any metal which is not a rare earth, transition metal, lanthanide or an actinide examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper, silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin, antimony, lead, and metals of the first, second and third groups of transition metals e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium, platinum, cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium etc.

Preferably $L\alpha$ is selected from β diketones such as those of formulae

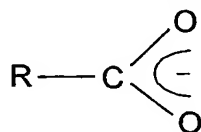


- where R_1 , R_2 and R_3 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures,

fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

- 5 Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

- 10 Some of the different groups L_α may also be the same or different charged groups such as carboxylate groups so that the group L_1 can be as defined above and the groups $L_2, L_3...$ can be charged groups such as



(IV)

- 15 where R is R_1 as defined above or the groups L_1, L_2 can be as defined above and $L_3...$ etc. are other charged groups.

R_1, R_2 and R_3 can also be



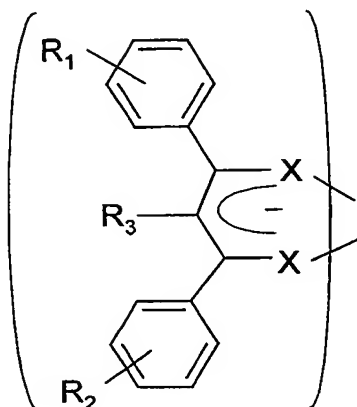
where X is O, S, Se or NH.

(V)

- 20 A preferred moiety R_1 is trifluoromethyl CF_3 and examples of such diketones are, benzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenathoyltrifluoroacetone, 3-phenanthoyltrifluoroacetone, 9-anthroyltrifluoroacetone, cinnamoyltrifluoroacetone, and 2-
25 thenoyltrifluoroacetone.

- 10 -

The different groups $L\alpha$ may be the same or different ligands of formulae

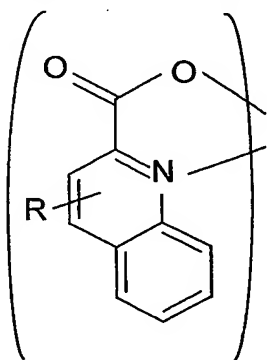


(VI)

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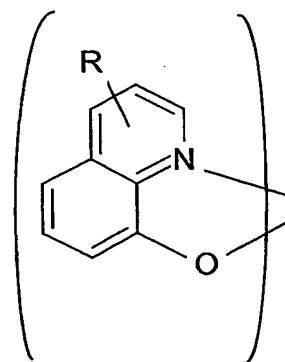
where X is O, S, or Se and R_1 , R_2 and R_3 are as above.

The different groups $L\alpha$ may be the same or different quinolate derivatives such as



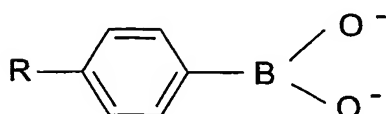
(VII)

or



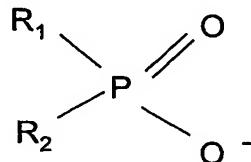
(VIII)

10 where R is hydrocarbyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy e.g. the 8 hydroxy quinolate derivatives or



(IX)

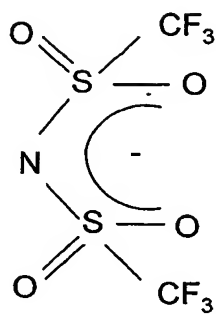
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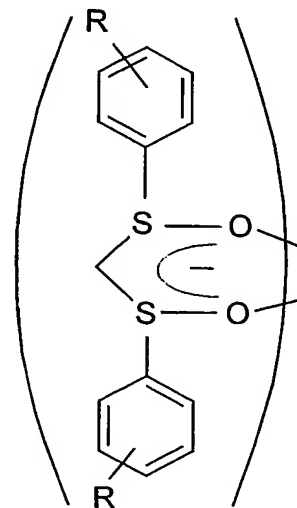
(X)

- 11 -

where R, R₁, and R₂ are as above or are H or F e.g. R₁ and R₂ are alkyl or alkoxy groups

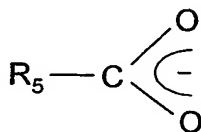


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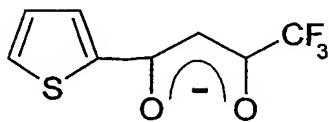
(XII)

- 5 As stated above the different groups L_α may also be the same or different carboxylate groups e.g.

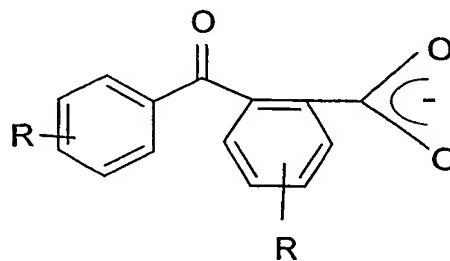


(XIII)

- where R₅ is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, R₅ can also be a 2-ethyl hexyl group so L_n is 2-ethylhexanoate or R₅ can be a chair structure so that L_n is 2-acetyl cyclohexanoate or L_α can be
- 10



(XIV)

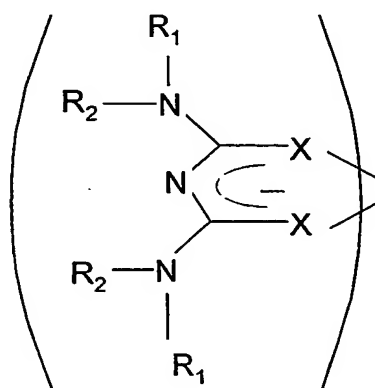


(XIVa)

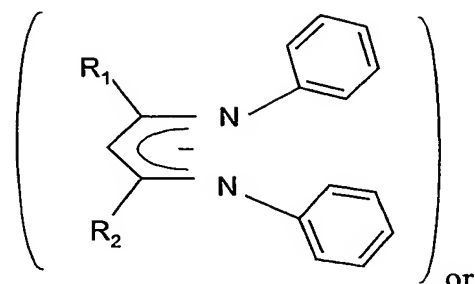
- 12 -

where R is as above e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring.

5 The different groups $L\alpha$ may also be



or

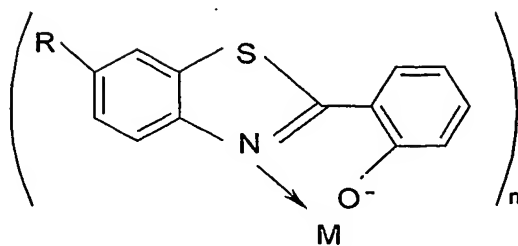


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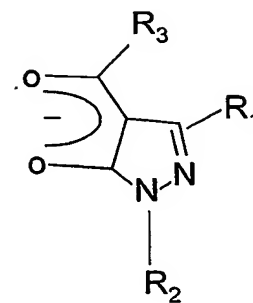
(XV)

(XVI)

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or



(XVII)

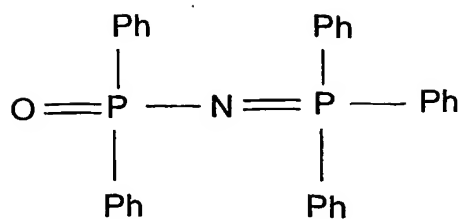
(XVIIa)

Where R , R_1 and R_2 are as above.

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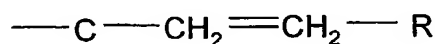
The groups L_p can be selected from

- 13 -



(XVIII)

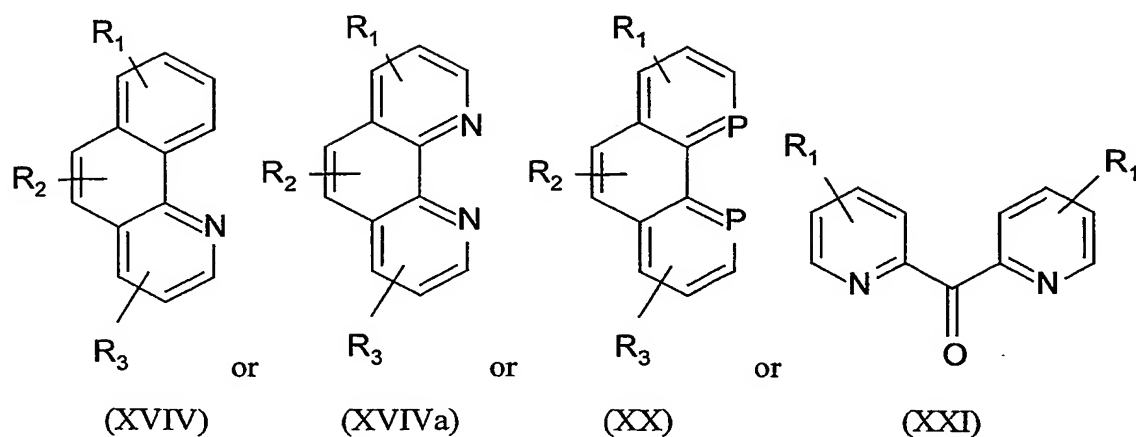
- where each Ph which can be the same or different and can be a phenyl (OPNP) or a substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polycyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene or pyrene group. The substituents can be for example an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polycyclic group, halogen such as fluorine, cyano, amino. Substituted amino etc. Examples are given in figs. 1 and 2 of the drawings where R, R₁, R₂, R₃ and R₄ can be the same or different and are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R, R₁, R₂, R₃ and R₄ can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. R, R₁, R₂, R₃ and R₄ can also be unsaturated alkylene groups such as vinyl groups or groups



where R is as above.

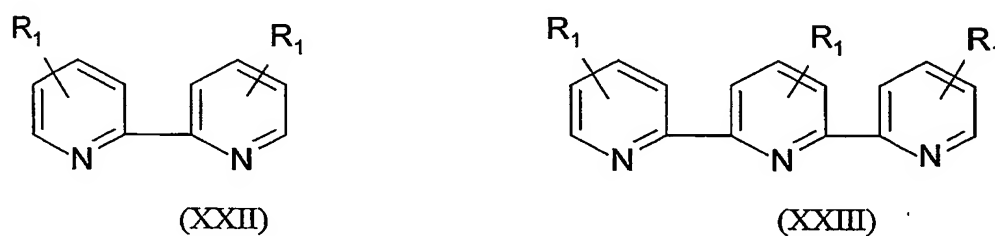
L_p can also be compounds of formulae

- 14 -



where R₁, R₂ and R₃ are as referred to above, for example bathophen shown in fig. 3 of the drawings in which R is as above or

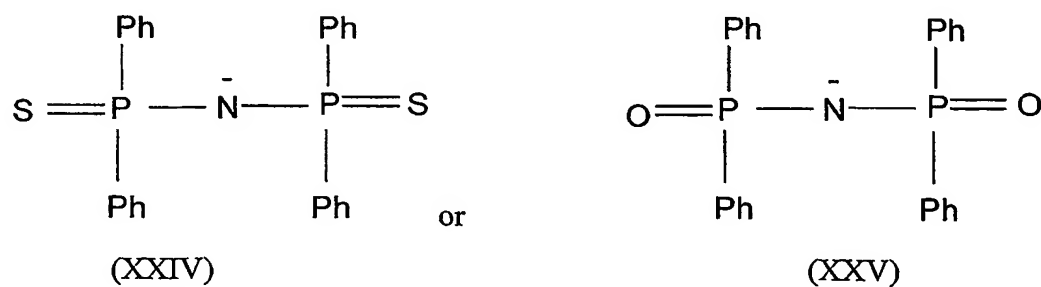
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where R₁, R₂ and R₃ are as referred to above.

10

L_p can also be



15 where Ph is as above.

- 15 -

Other examples of L_p chelates are as shown in figs. 4 and fluorene and fluorene derivatives e.g. a shown in figs. 5 and compounds of formulae as shown in figs. 6 to 8.

- 5 Specific examples of L_α and L_p are tripyridyl and TMHD, and TMHD complexes, α , α' , α'' tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA, where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 9.

10

Other electroluminescent materials which can be used include metal quinolates such as lithium quinolate, aluminium quinolate, scandium quinolate zirconium quinolate, hafnium quinolate vanadium quinolate etc. The quinolates can be doped e.g. with a dye such as diphenylquinacridine, diphenylquinacridone, coumarins, perylene and their derivatives.

15

- Other electroluminescent materials which can be used include organic complexes of non rare earth metals such as lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper, silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin, antimony, lead, and metals of the first, second and third groups of transition metals e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium, platinum, cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium etc. which emit light when an electric current is passed through it. The complexes can be formed with the ligands of formula (I) to (XVII) above, optionally with a neutral ligand of formula L_p as defined above.

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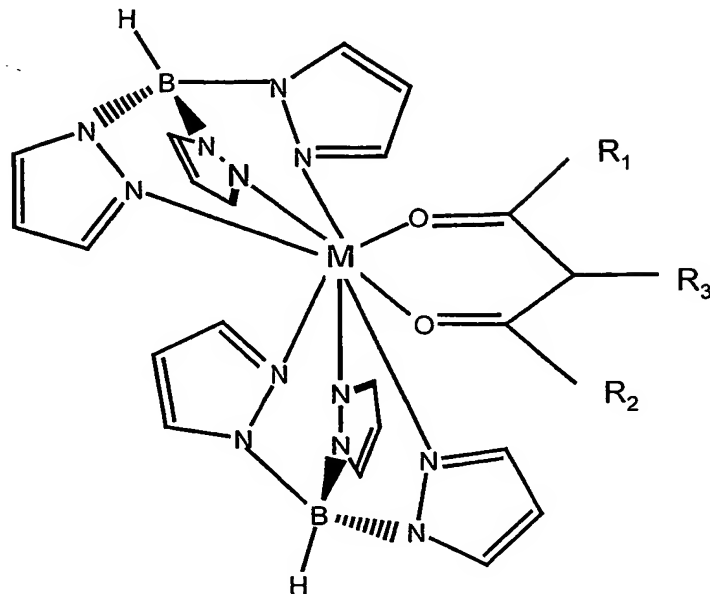
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- Such complexes are complexes of β -diketones e.g. tris -(1,3-diphenyl-1,3-propanedione) (DBM) and suitable metal complexes are $Al(DBM)_3$, $Zn(DBM)_2$ and $Mg(DBM)_2$, $Sc(DBM)_3$ etc.

30

- 16 -

Further complexes which can be used as the photovoltaic element are borate complexes of formula



where M is a rare earth, lanthanide or an actinide and R_1 , R_2 and R_3 are as defined above.

A photovoltaic device can be made in the conventional way for example by forming a layer of the metal chelate on a metal so the metal forms a first electrode and preferably the other, second electrode, comprises a transparent conductive layer. This electrode is preferably a transparent substrate which is a conductive glass or plastic material which acts as the cathode; preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used, so that, when light falls on the metal chelate an electric field is generated between the electrodes.

15

There are a very large number of designs for photovoltaic devices and solar cells and a survey of such devices is given in the Jean-Michel Nunzi Article referred to above and in the references thereto. In general the metal chelates can be used as the photovoltaic element in such devices.

- 17 -

The metal chelate material can be deposited on the metal or conductive transparent material substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend on the material, but
5 chlorinated hydrocarbons such as dichloromethane, n-methyl pyrrolidone, dimethyl sulphoxide, tetra hydrofuran dimethylformamide etc. are suitable in many cases.

Alternatively the material can be deposited by spin coating from solution or by vacuum deposition from the solid state e.g. by sputtering or any other conventional
10 method can be used.

As stated above, the electrons by absorption of solar radiation of the appropriate bandgap, produce electron-hole pairs. The separation of the electron-hole pairs with the electrons flowing toward the region of N-type conductivity, and the holes flowing
15 toward the region of P-type conductivity, creates the photovoltage and photocurrent of the cell. By having a layer of a hole transmitting material, i.e. a p-type transmitter between the cathode and the metal chelate and/or a layer of an electron transmitting material between the metal chelate and the anode, increased mobility of the holes and the electrons can be achieved increasing the effectiveness of the photovoltaic cell.

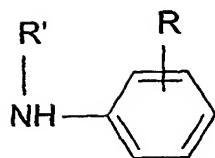
20

Hole transmitting layers are used in polymer electroluminescent devices and any of the known hole transmitting materials in film form can be used.

The hole transporting material can be an amine complex such as poly
25 (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of

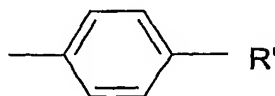
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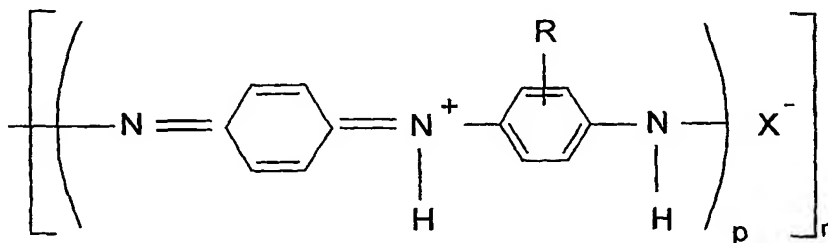
(XXVI)

- 5 where R is in the ortho – or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



- 10 where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above.

Or the hole transporting material can be a polyaniline. Polyanilines which can be used in the present invention have the general formula



(XXVII)

- 15 where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO₄, BF₄, PF₆, H₂PO₃, H₂PO₄, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate
- 20 alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate; an example of an arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

5

We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the unsubstituted or substituted polymer of an amino substituted aromatic compound is
10 deprotonated then it can be easily evaporated i.e. the polymer is evaporable.

Preferably evaporable deprotonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated unsubstituted or substituted polymer of an amino substituted aromatic compound can
15 be formed by deprotonating the polymer by treatment with an alkali such as ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

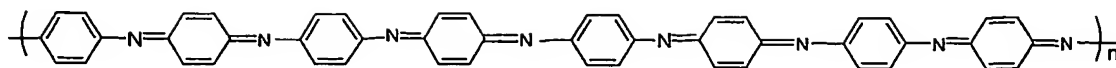
The degree of protonation can be controlled by forming a protonated polyaniline and
20 de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60%
25 e.g. about 50%.

Preferably the polymer is substantially fully deprotonated.

A polyaniline can be formed of octamer units i.e. p is four e.g.

- 20 -



The polyanilines can have conductivities of the order of 1×10^{-1} Siemen cm^{-1} or higher.

5

The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

10

The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

15

Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in US Patent 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a group R as defined above.

20

Other hole transporting materials are conjugated polymer and the conjugated polymers which can be used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

25

The preferred conjugated polymers are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy)-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy)-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes)

- 21 -

with at least one of the alkoxy groups being a long chain solubilising alkoxy group, polyfluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

- 5 In PPV the phenylene ring may optionally carry one or more substituents e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

- Any poly(arylenevinylene) including substituted derivatives thereof can be used and
10 the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthylene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.

- The conjugated polymers can be made by the methods disclosed in US 5807627,
15 PCT/WO90/13148 and PCT/WO92/03490.

The thickness of the hole transporting layer is preferably 20nm to 200nm.

- The polymers of an amino substituted aromatic compound such as polyanilines
20 referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.

- The structural formulae of some other hole transporting materials are shown in
Figures 12, 13, 14, 15 and 16 of the drawings, where R_1 , R_2 and R_3 can be the same or
25 different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic
30 and polycyclic ring structures and can be copolymerisable with a monomer e.g.

- 22 -

styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

5

Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and unsubstituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

10

Optionally there is a layer of an electron injecting material between the anode and the electroluminescent material layer; the electron injecting material is a material which will transport electrons when an electric current is passed through it; electron injecting materials include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate, a cyano anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 9 or 10 of the drawings in which the phenyl rings can be substituted with substituents R as defined above.

20

The cathode is preferably a transparent substrate such as a conductive glass or plastic material which acts as the anode. Preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer such as a metal or conductive polymer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.

25

The anode is preferably a low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys, rare earth metal alloys etc., aluminium is a preferred metal.

A metal fluoride such as an alkali metal, rare earth metal or their alloys can be used as the second electrode for example by having a metal fluoride layer formed on a metal.

- 5 As stated above, the photocurrent output of a solar cell is maximized by increasing the total number of photons of differing energy and wavelength which are absorbed by the semiconductor material and it is a feature of the present invention that the rare earth metal chelates can absorb light of a specific wavelength depending on the metal and ligands used so, by having a plurality of layers of different metal chelates of
- 10 differing bandgaps which absorb light at different wavelengths, a wide range of the visible spectrum can be used. Metal chelates can be also used which will absorb light in the infra-red, ultra-violet or shorter wavelengths so improving the utilisation of sunlight and increasing the power achievable by a solar cell.
- 15 As stated above, the photocurrent output of a solar cell is maximized by increasing the total number of photons of differing energy and wavelength which are absorbed by the semiconductor material and it is a feature of the present invention that the rare earth metal chelates can absorb light of a specific wavelength depending on the metal and ligands used so, by having a plurality of layers of different metal chelates of
- 20 differing bandgaps which absorb light at different wavelengths, a wide range of the visible spectrum can be used. Metal chelates can be also used which will absorb light in the infra-red, ultra-violet or shorter wavelengths so improving the utilisation of sunlight and increasing the power achievable by a solar cell.
- 25 Alternatively individual solar cells of differing bandgap energies i.e. using different metal chelates of differing bandgaps which absorb light at different wavelengths can be connected in series.

Devices of the invention are illustrated in the drawings in which:-

Fig. 17 shows a simple photovoltaic cell

Figs. 18 and 19 show other cells and

Fig. 20 shows a tandem cell

5

Referring to fig. 17 a simple cell comprises a metal anode e.g. made of aluminium (1) a layer of an electroluminescent material (2) as described herein and a cathode comprising an indium titanium oxide (ITO) coated glass (3). When light passes through the ITO coated glass it is absorbed by the electroluminescent material layer (2), which is the photovoltaic element, and an electric field is generated between the anode and cathode and when the anode and cathode are connected through an electric circuit an electric current will flow between them.

10

Referring to fig. 18 there is a layer of an electron transmitting material (4) between the layers (2) and (1).

15

Referring to fig. 19 there is a layer of a hole transporting layer (5) between the layers (2) and (3).

Referring to fig. 20 this shows a tandem solar cell in which there are a plurality of cells in series of fig. 17 formed of a cathode (11), an electroluminescent layer (13) and anode (12) so that a larger field is generated between the end anode and cathode, in order for there to be a transmission of light through the cells the anodes and cathodes of the intermediate cells are transparent. At least some of the photovoltaic elements (13) in each of the cells are different to adsorb light at a range of wavelengths.

20

Example 1

A photovoltaic device was fabricated on a clean and dried ITO coated glass piece (1 x 1cm²) by sequentially forming layers by vacuum evaporation to form a structure

30

- 25 -

ITO/CuPc(20nm)/TPD(50nm)/ Eu (DBM)₃(OPNP)/(85nm)Alq₃/LiF(0.4nm)/Al

5 Where CuPc is copper phthalocyanine, TPD is N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine, Alq₃ is aluminium quinolate, LiF is lithium fluoride and Al is aluminium.

10 To deposit the layers the organic coating on the portion which had been etched with the concentrated hydrochloric acid was wiped with a cotton bud. The coated electrodes were stored in a vacuum desiccator over a molecular sieve and phosphorous pentoxide until they were loaded into a vacuum coater (Edwards, 10⁻⁶ torr) and aluminium top contacts made. The active area of the photovoltaic device was 0.08 cm by 0.1 cm² the devices were then kept in a vacuum desiccator until the photovoltaic studies were performed.

15

The device was connected in an electric circuit and exposed to light of various wavelengths λ and the voltage and current measured the results are shown graphically in fig. 21 where the open circuit voltage Voc and short circuit current Jsc (as described in the Jean-Michel Nunzi Article referred to above) were obtained. The white light was obtained from a simulated daylight fluorescent bulb.

20

Example 2

Example 1 was repeated using a structure comprising

25

ITO/CuPc(20nm)/ α -NPB(75nm)/Zrqa₄:DPQA(75:0.75nm)/Zrqa₄10nm)Alq₃/LiF(0.4nm)/Al

Where α -NPB is as shown in fig. 16a, DPQA is diphenylquinacridone.

- 26 -

The Zrq₄ is zirconium quinolate and the Zrq₄:DPQA layer was formed by concurrent vacuum deposition to form a zirconium quinolate layer doped with DPQA. The weight ratio of the Zrq₄ and DPQA is conveniently shown by a relative thickness measurement.

5

The device was connected in an electric circuit and exposed to light of various wavelengths λ and the voltage and current measured the results are shown graphically in fig. 22 where the open circuit voltage Voc and short circuit current Jsc (as described in the Jean-Michel Nunzi Article referred to above) were obtained. The

10

white light was obtained from a simulated daylight fluorescent bulb.

Example 3

Example 1 was repeated using a structure comprising

15

ITO/CuPc(20nm)/ α -NPB(75nm)/Liq(65nm)/Al.

Where Liq is lithium quinolate

20

The device was connected in an electric circuit and exposed to light of various wavelengths λ and the voltage and current measured the results are shown graphically in fig. 23 where the open circuit voltage Voc and short circuit current Jsc (as described in the Jean-Michel Nunzi Article referred to above) were obtained. The white light was obtained from a simulated daylight fluorescent bulb.

25

Example 4

Example 1 was repeated using a structure comprising

- 27 -

ITO/CuPc(20nm)/ α -NPB(75nm)/Liq(65nm)/LiF(0.4nm)/Al.

The device was connected in an electric circuit and exposed to light of various wavelengths λ and the voltage and current measured the results are shown graphically in fig. 24 where the open circuit voltage V_{oc} and short circuit current J_{sc} (as described in the Jean-Michel Nunzi Article referred to above) were obtained. The white light was obtained from a simulated daylight fluorescent bulb.

Example 5

10

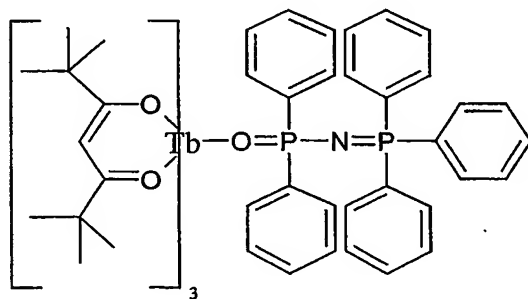
Devices were made as in Example 1 of structure

ITO/CuPc(25)/ α -NPB(80)/CBP:Compound A(30:2)/BCP(10)/Zr_q4(60)/LiF(0.2)/Al

Where the film thicknesses are in nanometres and CBP is as in fig. 4b and BCP is bathocupron

15

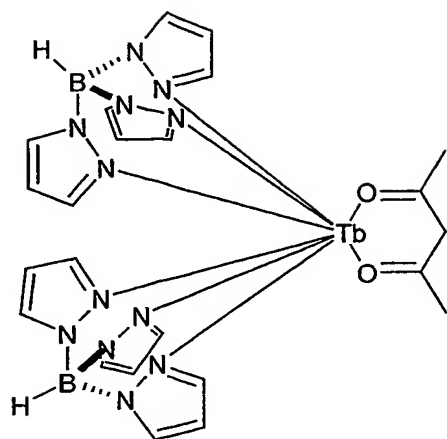
compound A was



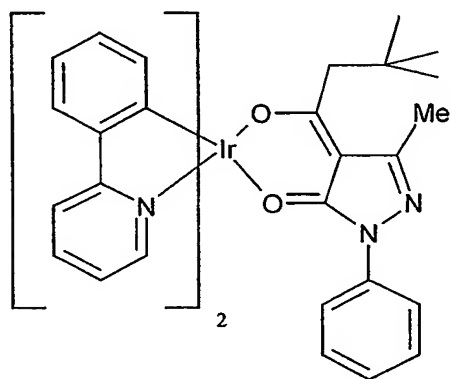
Similar devices were made with compounds B and C in place of compound A where compound B is

20

- 28 -



and compound C is



5

The results are shown in the Table

Table

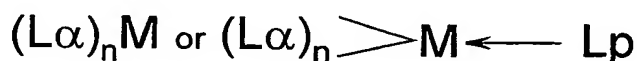
Photovoltaic element	$V_{\text{Ph}}^{\text{OC}} / \text{mV}$	$J_{\text{Ph}}^{\text{SC}} / \text{mA cm}^{-2}$	λ / nm
A	7.5	- 0.4	600
B	-0.3	2.2	500
C	-159	0.4	550

10

- 29 -

Claims

1. A photovoltaic device comprising a metal chelate as the photovoltaic element.
- 5 2. A photovoltaic device as claimed in claim 1 which comprises sequentially (i) a first electrode comprising a metal, (ii) the photovoltaic element and (iii) a second electrode.
3. A device as claimed in claim 1 or 2 in which the photovoltaic element comprises
- 10 an organo metallic complex of formula



- where $L\alpha$ and Lp are organic ligands, M is a metal and n is the valence state of the metal M and in which the ligands $L\alpha$ are the same or different.

4. A device as claimed in any one of claims 1 to 4 in which the metal M is a rare earth, transition metal, lanthanide or an actinide.
- 20 5. A device as claimed in claim 4 in which the said rare earth, transition metal, lanthanide or an actinide is selected from $Sm(III)$, $Eu(II)$, $Eu(III)$, $Tb(III)$, $Dy(III)$, $Yb(III)$, $Lu(III)$, $Gd(III)$, $Gd(III)$, $U(III)$, $Tm(III)$, $Ce(III)$, $Pr(III)$, $Nd(III)$, $Pm(III)$, $Dy(III)$, $Ho(III)$ and $Er(III)$.
- 25 6. A device as claimed in any one of claims 1 to 3 in which the metal M is a non rare earth metal.
7. A device as claimed in claim 6 in which the metal M is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium,

- 30 -

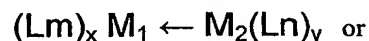
barium, copper, silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin, antimony, lead, and metals of the first, second and third groups of transition metals, manganese, iron, ruthenium, osmium, cobalt, nickel, palladium, platinum, cadmium, chromium, titanium, vanadium, zirconium, tantalum,
 5 molybdenum, rhodium, iridium, titanium, niobium, scandium and yttrium.

8. A device as claimed in any one of claims 3 to 7 in which there are a plurality of ligands L_p which can be the same or different.

10 9. A device as claimed in any one of the preceding claims in which the photovoltaic element comprises an organo metallic complex of formula $(L_n)_n M_1 M_2$ or $(L_n)_n M_1 M_2 (L_p)_z$, where L_n is L_α , L_p is a neutral ligand M_1 is a rare earth, transition metal, lanthanide or an actinide, M_2 is a non rare earth metal and n is the combined valence state of M_1 and M_2 .

15

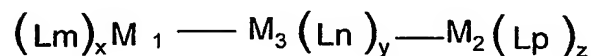
10. A device as claimed in any one of the preceding claims in which the photovoltaic element comprises a binuclear, trinuclear or polynuclear organometallic complex of formula



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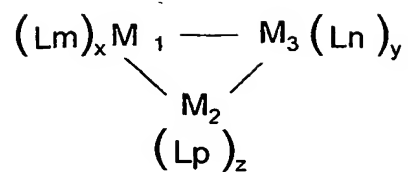
where L is a bridging ligand and where M_1 is a rare earth metal and M_2 is M_1 or a non rare earth metal, L_m and L_n are the same or different organic ligands L_α as defined above, x is the valence state of M_1 and y is the valence state of M_2 or

25

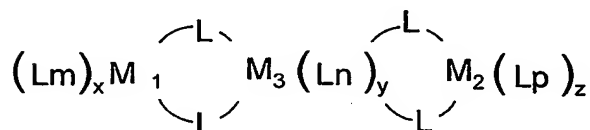


or

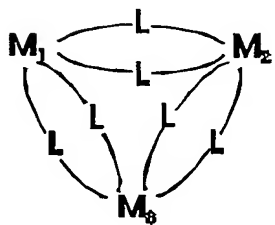
- 31 -



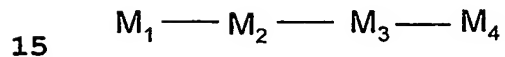
- 5 where M_1 , M_2 and M_3 are the same or different rare earth metals and Lm , Ln and Lp are organic ligands $\text{L}\alpha$ and x is the valence state of M_1 , y is the valence state of M_2 and z is the valence state of M_3 and Lp can be the same as Lm and Ln or different or



10 or

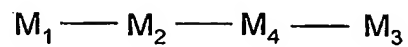


or



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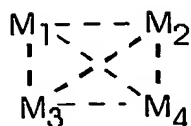
or



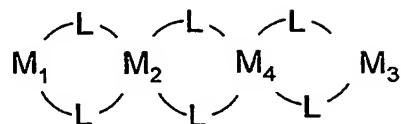
or

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- 32 -



or



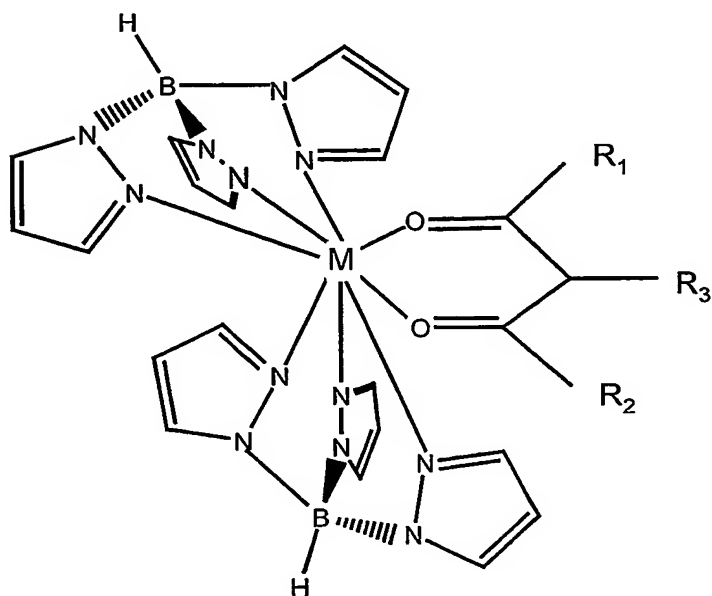
- 5 where M_4 is M_1 and L is a bridging ligand and in which the rare earth metals and the non rare earth metals can be joined together by a metal to metal bond and/or via an intermediate bridging atom, ligand or molecular group or in which there are more than three metals joined by metal to metal bonds and/or via intermediate ligands and
- 10 11. A device as claimed in any one of claims 3 to 10 in which $L\alpha$ has the formula (I) to (XVII) herein.
12. A device as claimed in any one of claims 3 to 11 in which Lp has the formula of figs. 1 to 8 of the accompanying drawings or of formula (XVIII) to (XXV) herein.
- 15 13. A device as claimed in claim 1 or 2 in which the organometallic chelate is a metal quinolate.
14. A device as claimed in claim 13 in which the metal quinolate is lithium quinolate, aluminium quinolate, scandium quinolate zirconium quinolate, hafnium quinolate or vanadium quinolate.
- 20 15. A device as claimed in claim 14 in which the metal quinolate is doped with a fluorescent, phosphorescence or ion fluorescent compound.

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- 33 -

16. A device as claimed in claim 15 in which the dopant is diphenylquinacridine, diphenylquinacridone, coumarins, perylene or their derivatives.

17. A device as claimed in claim 1 or 2 in which the photovoltaic element has the
5 formula



where M is a rare earth, transition metal, lanthanide or an actinide and R₁, R₂ and R₃
10 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups, substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons and trifluoromethyl groups, halogens and thiophenyl groups.

18. A device as claimed in any one of claims 2 to 17 in which the second electrode
15 comprises a transparent substrate which is a conductive glass or plastic material and which covers at least part of the photovoltaic element.

- 34 -

19. A device as claimed in any one of the preceding claims which comprises sequentially (i) a first electrode comprising a metal, (ii) a plurality of layers of photovoltaic elements in which the photovoltaic elements in at least two of the layers are different and (iii) a second electrode.

5

20. A device as claimed in claim 19 in which at least some of the different photovoltaic elements absorb light at different wavelengths.

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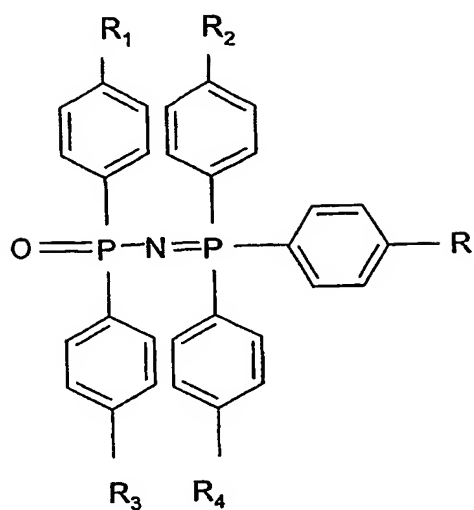


Fig. 1

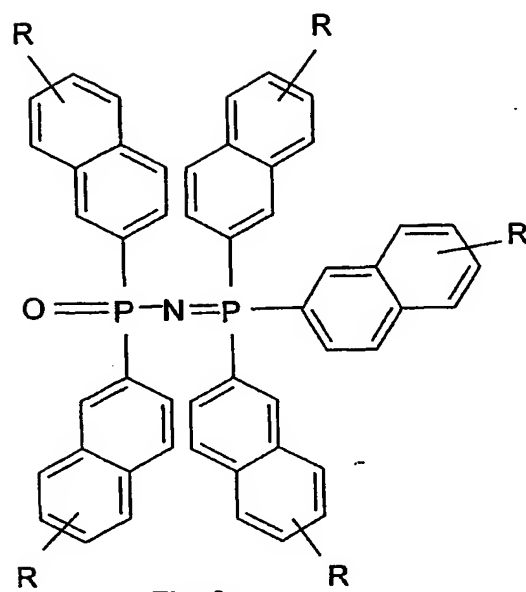


Fig. 2a

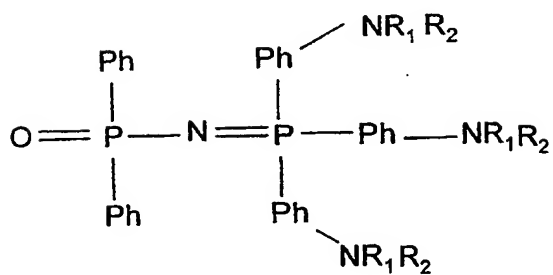


Fig. 2b

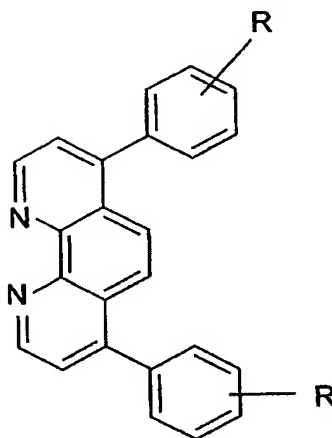


Fig. 3

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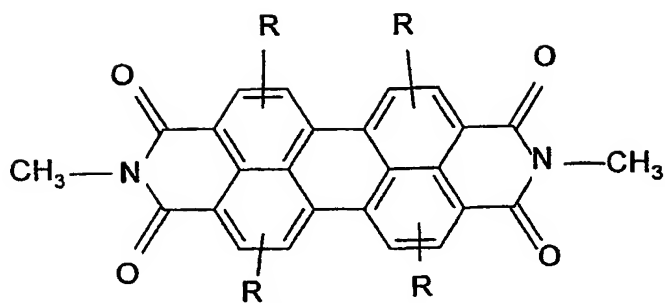


Fig. 4a

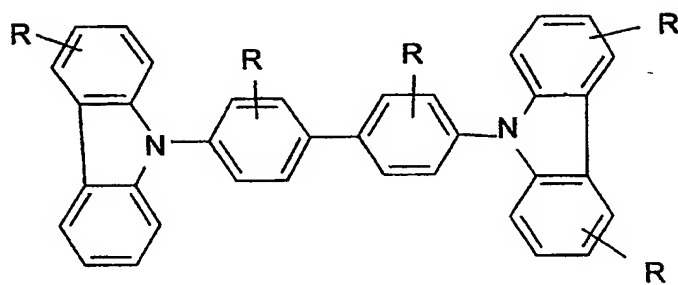


Fig. 4b

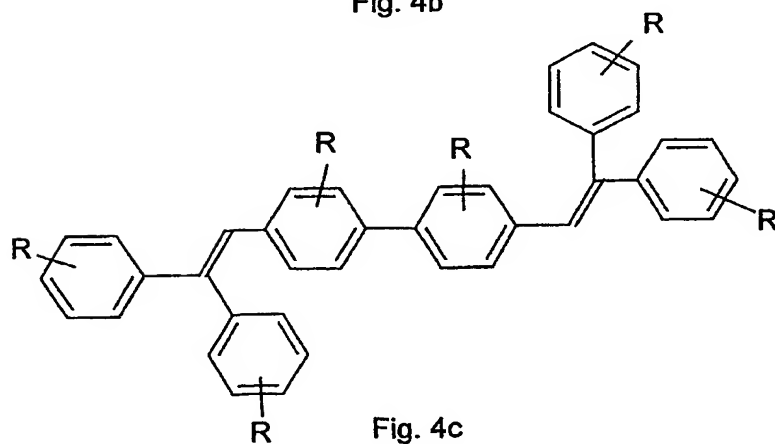


Fig. 4c

3/24

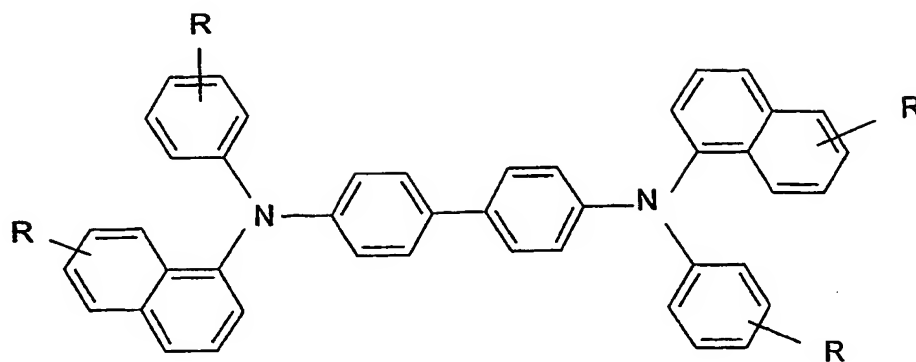


Fig. 4d

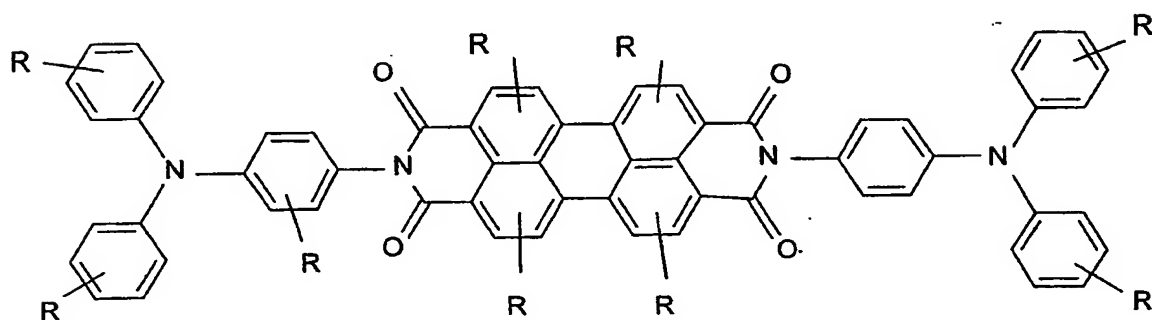


Fig. 4e

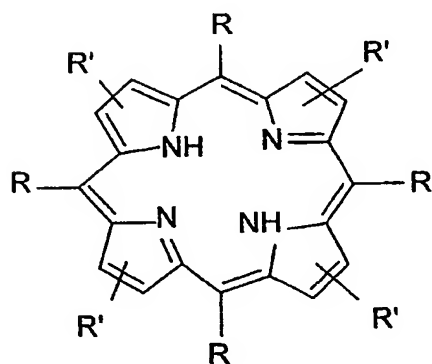


Fig. 4f

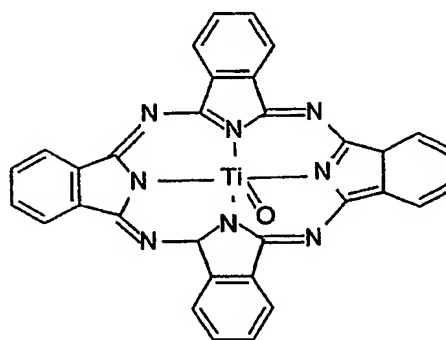


Fig. 4g

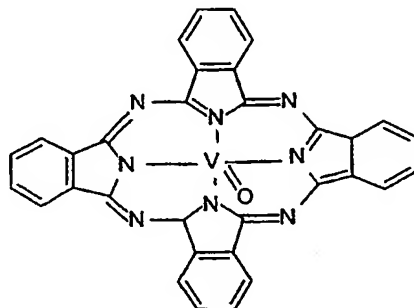


Fig. 4h

4/24

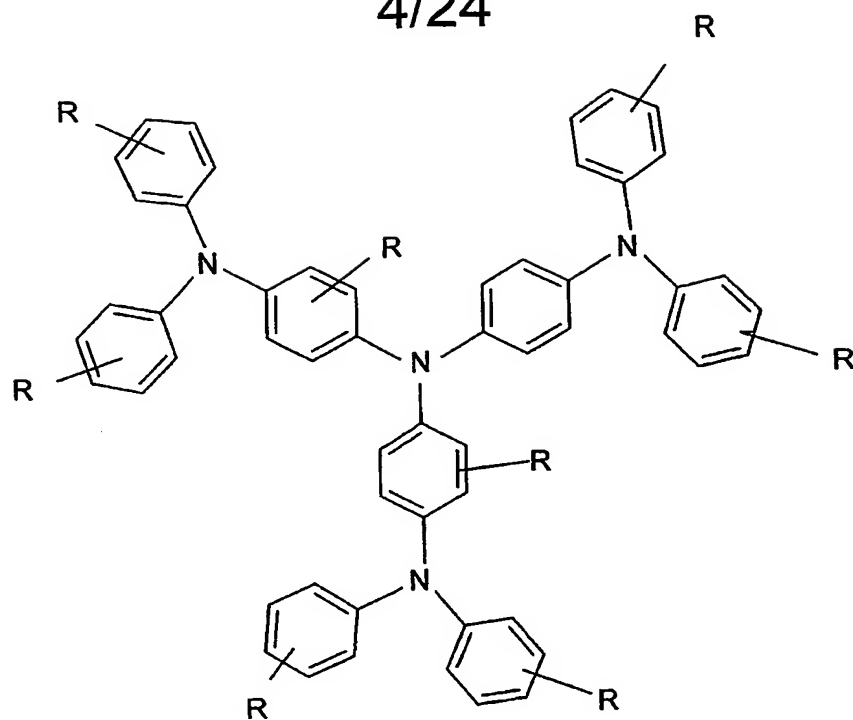


Fig. 4i

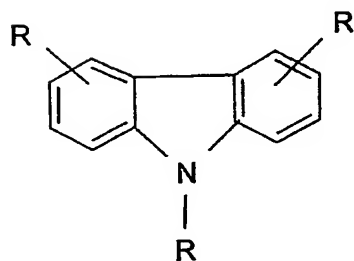


Fig. 4j

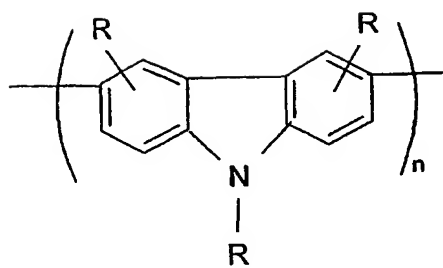


Fig. 4k

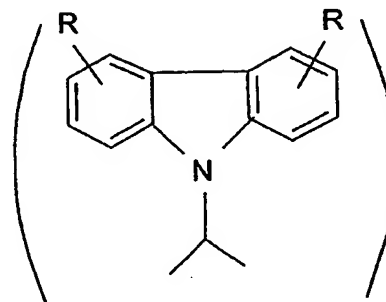


Fig. 4l

5/24

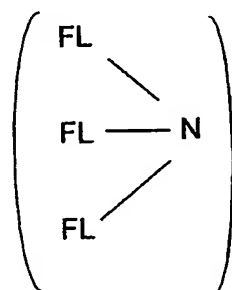


Fig. 5a

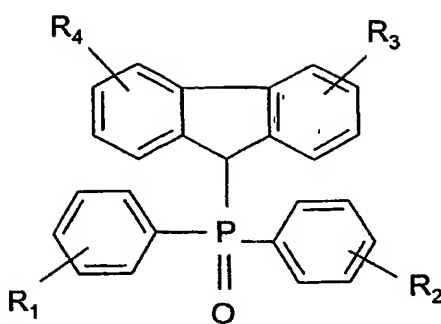


Fig. 5b

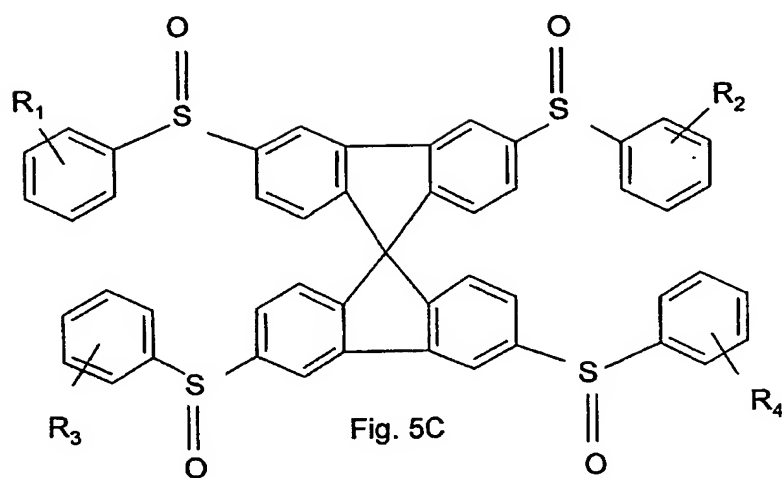


Fig. 5c

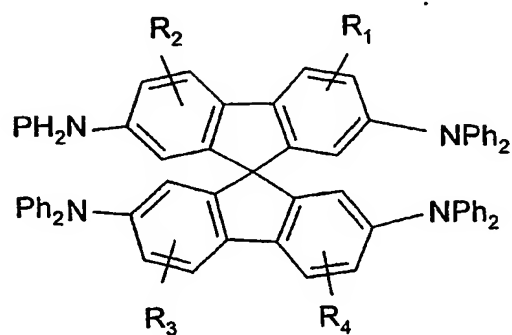


Fig. 5d

6/24

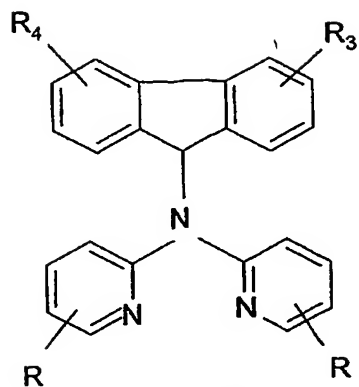


Fig. 5e

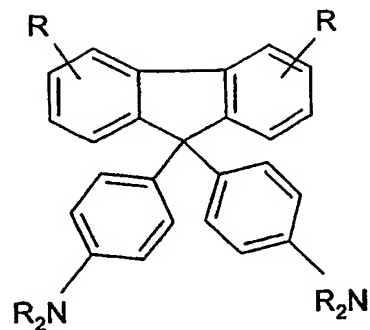


Fig 5f

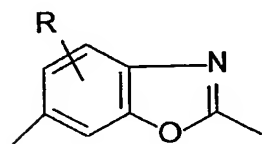


Fig. 6a

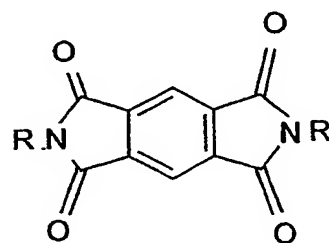


Fig 6b

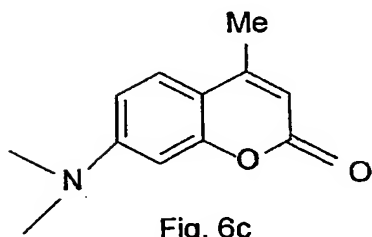


Fig. 6c

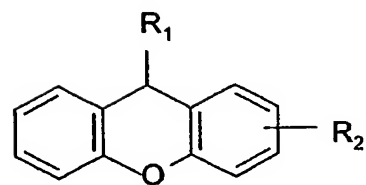


Fig. 6d

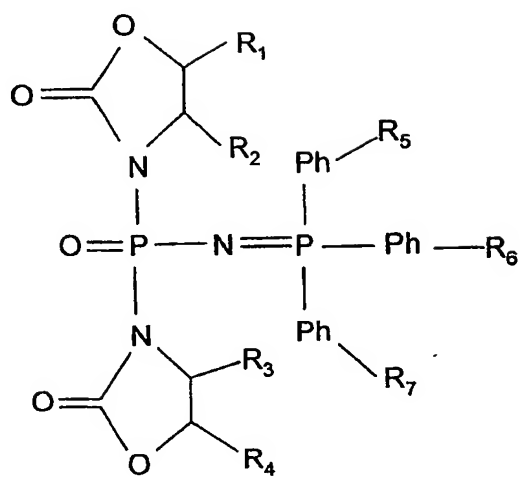


Fig. 6e

7/24

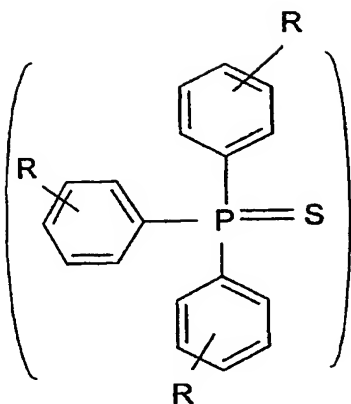


Fig. 7a

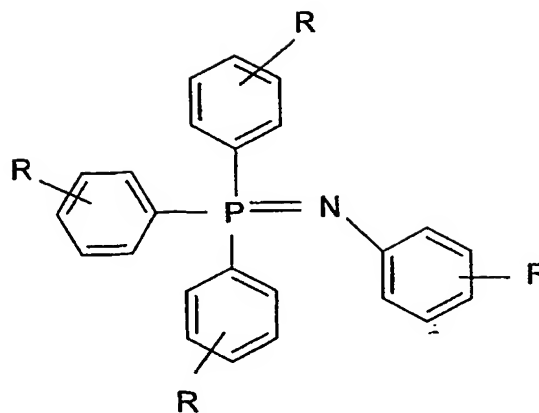


Fig. 7b

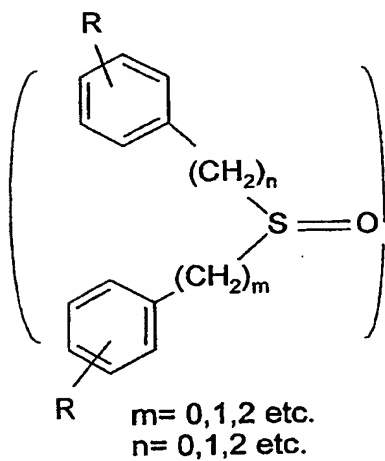


Fig. 7c

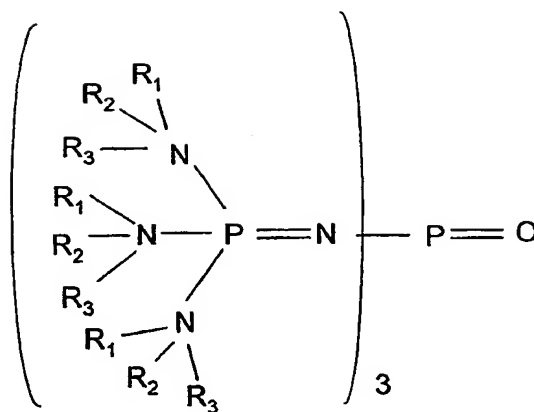


Fig. 7d

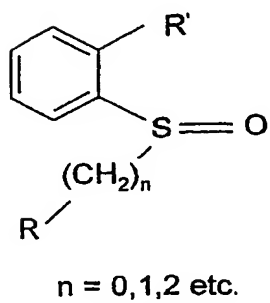


Fig. 7e

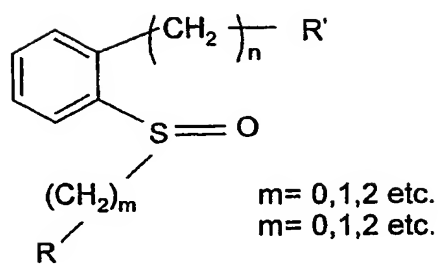


Fig. 7f

8/24

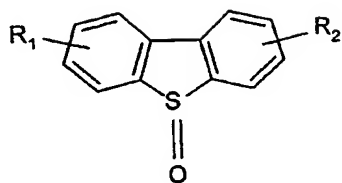


Fig. 8a

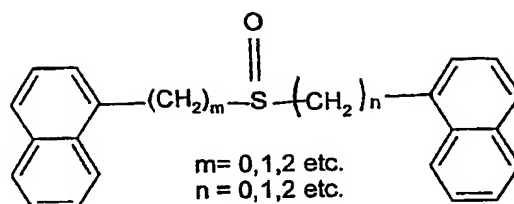


Fig. 8b

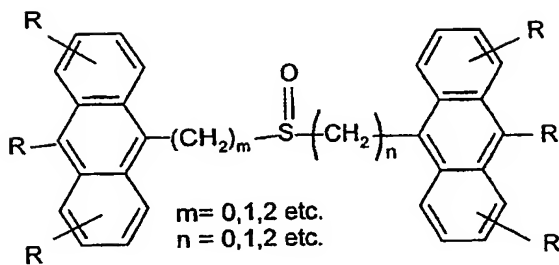


Fig. 8c

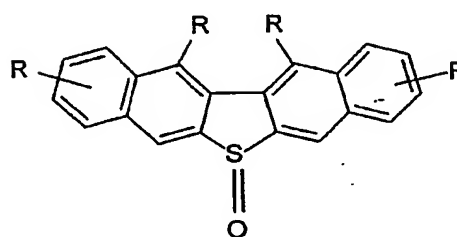


Fig. 8d

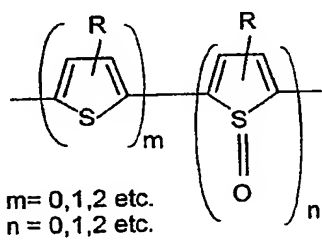


Fig. 8e

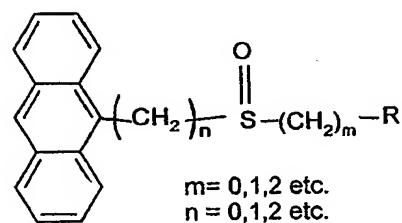


Fig. 8f

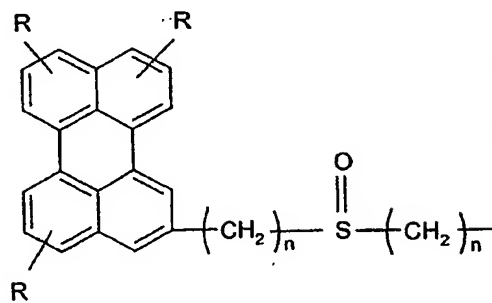


Fig. 8g

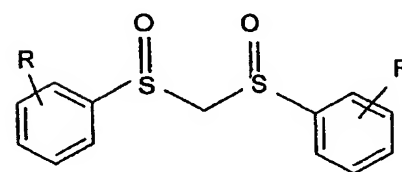
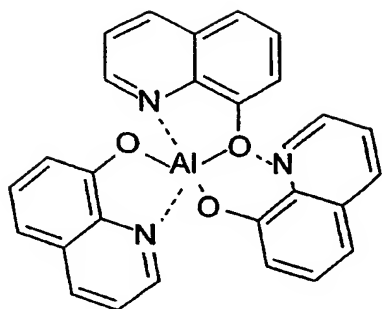
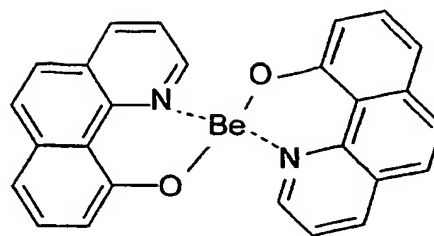


Fig. 8h

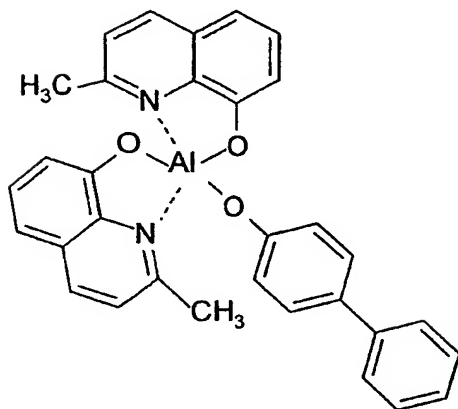
9/24



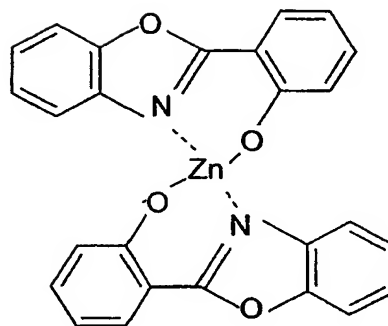
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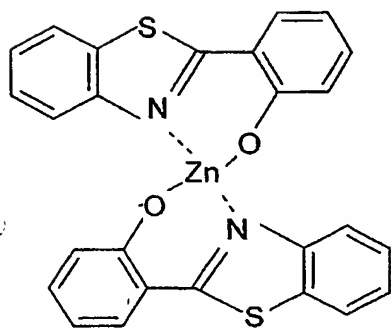
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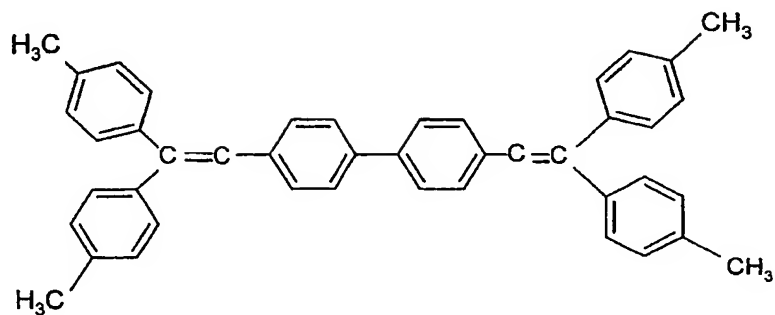
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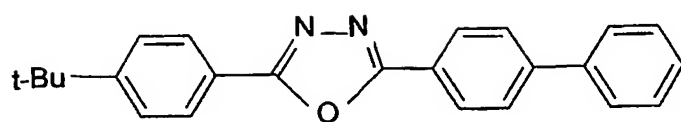
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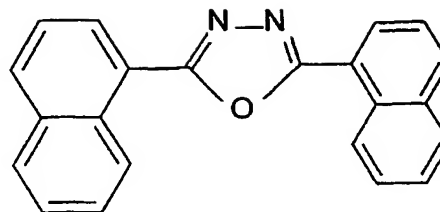
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Fig. 9

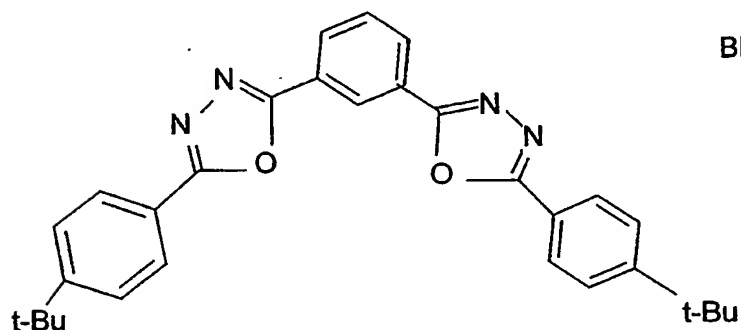
10/24



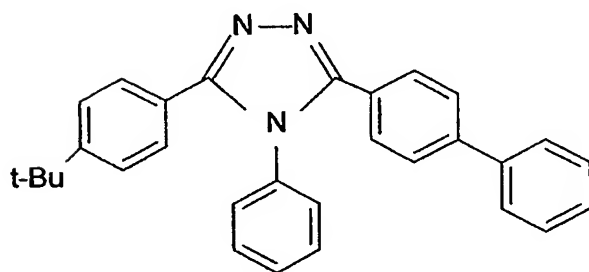
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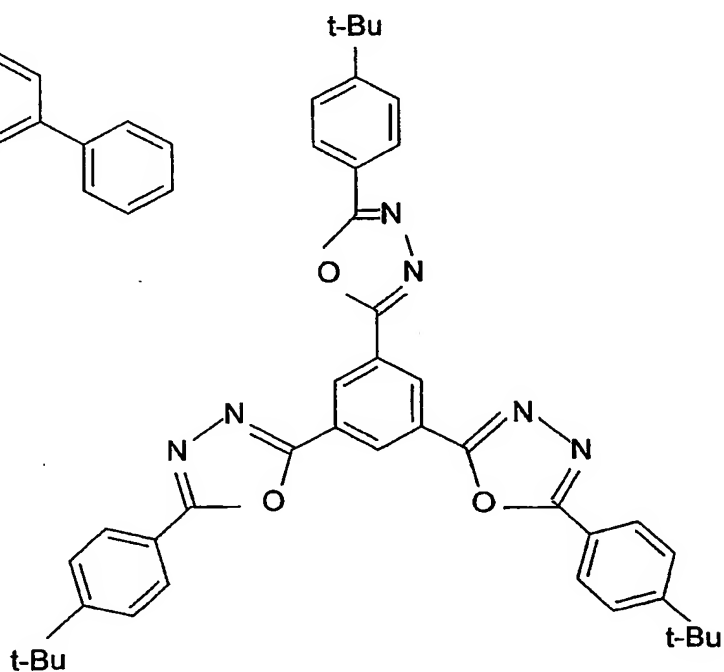
BND



OXD-7



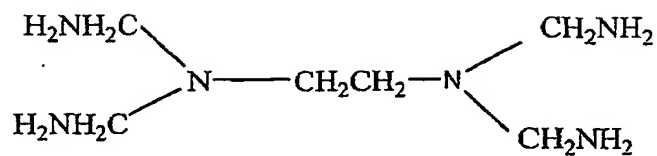
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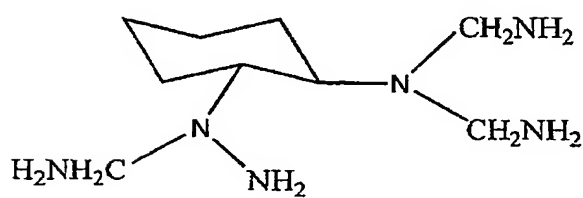
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Fig. 10

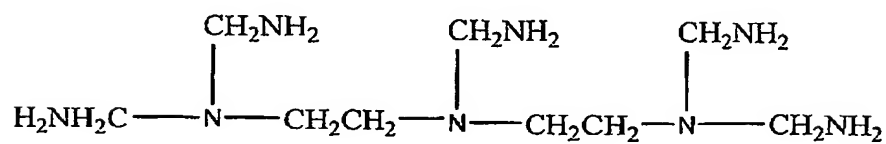
11/24



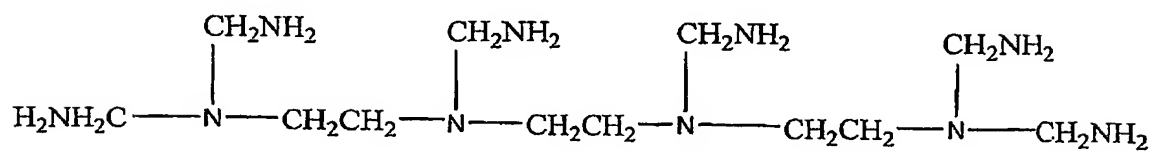
EDTA



DCTA



DTPA



TTHA

Fig. 11

12/24

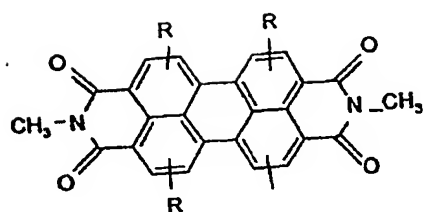


Fig. 12a

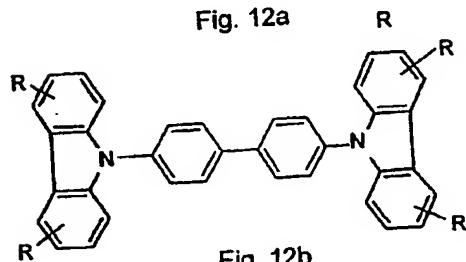


Fig. 12b

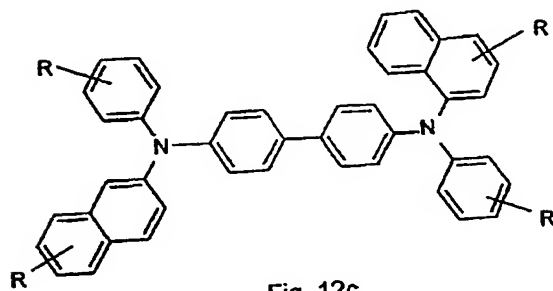


Fig. 12c

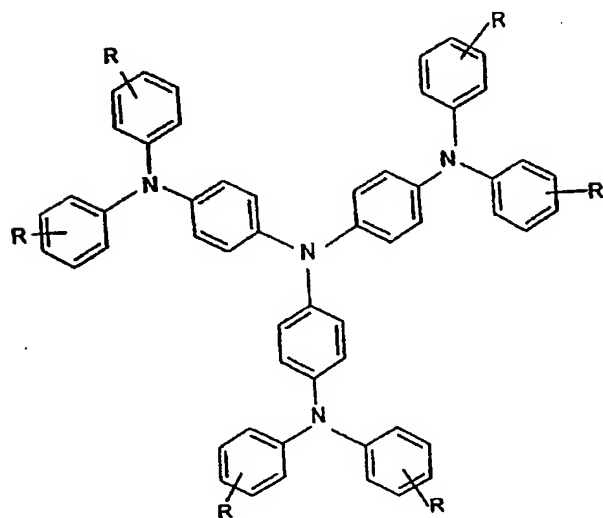


Fig. 12d

13/24

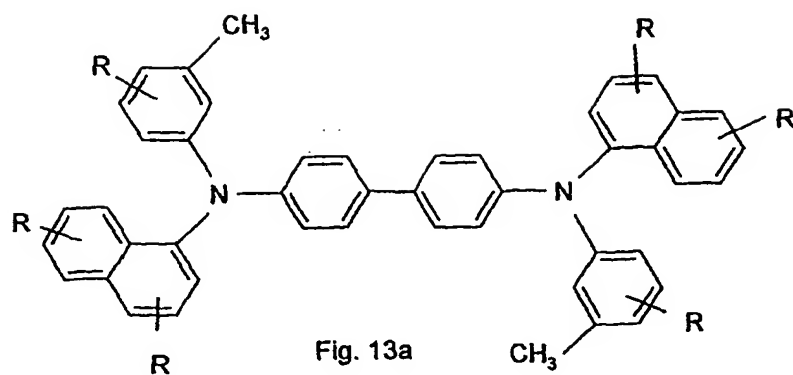


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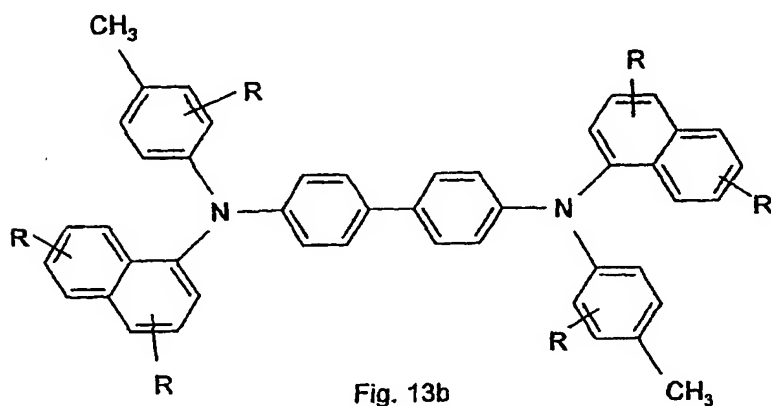


Fig. 13b

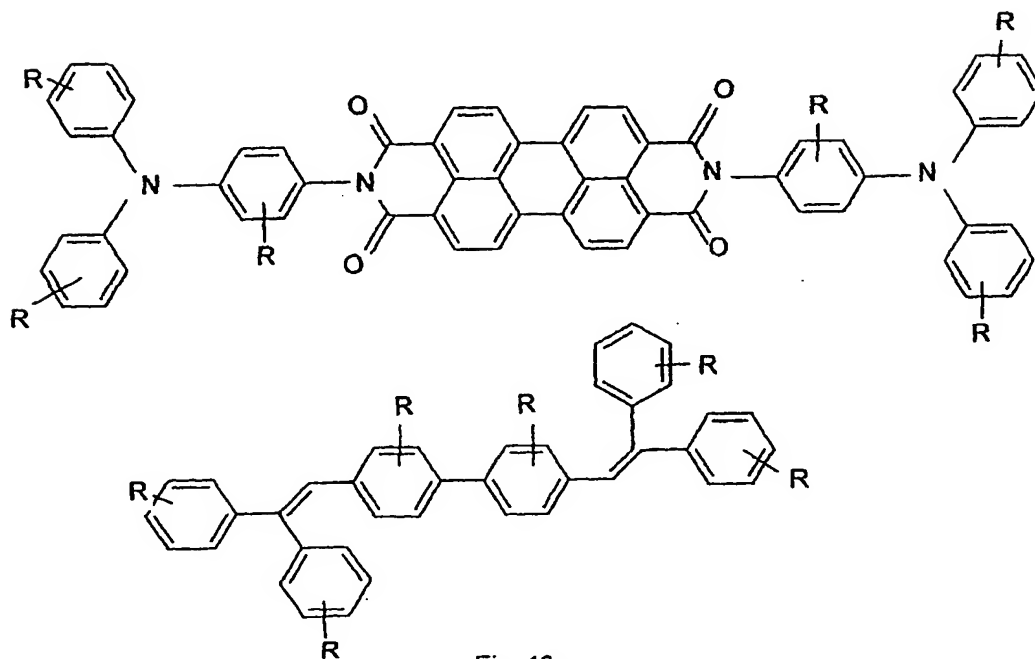


Fig. 13c

14/24

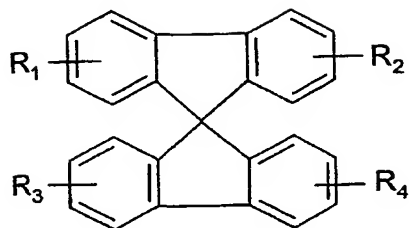


Fig. 14a

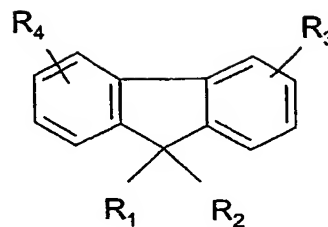
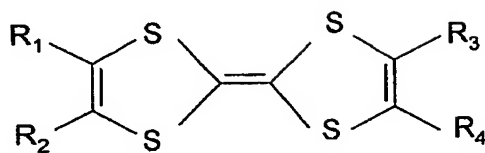


Fig. 14b



or

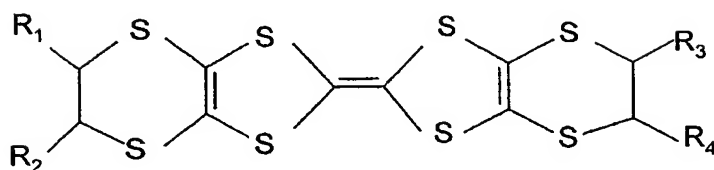


Fig. 14c

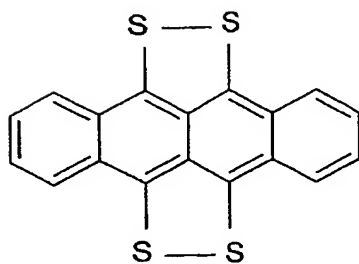


Fig. 14d

15/24

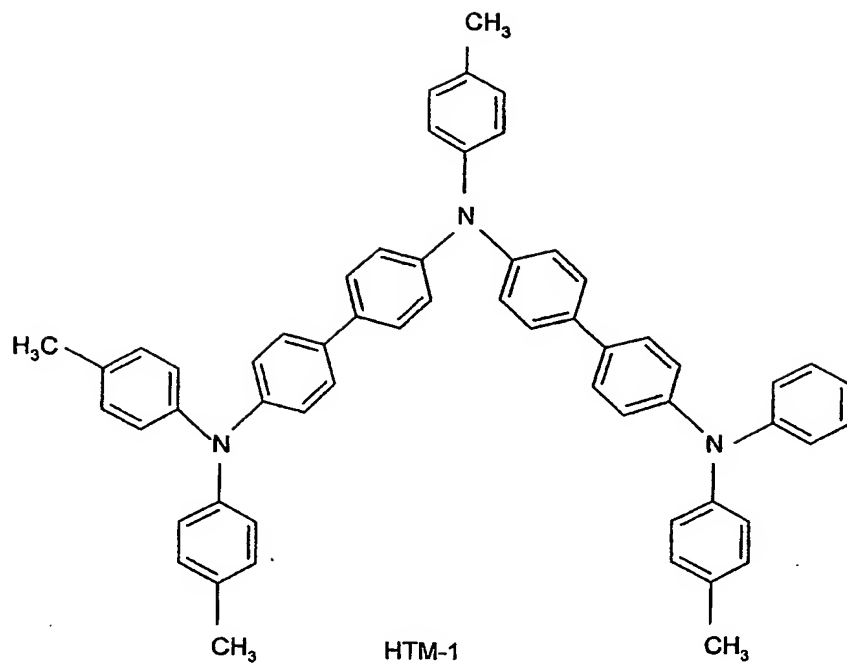


Fig. 15a

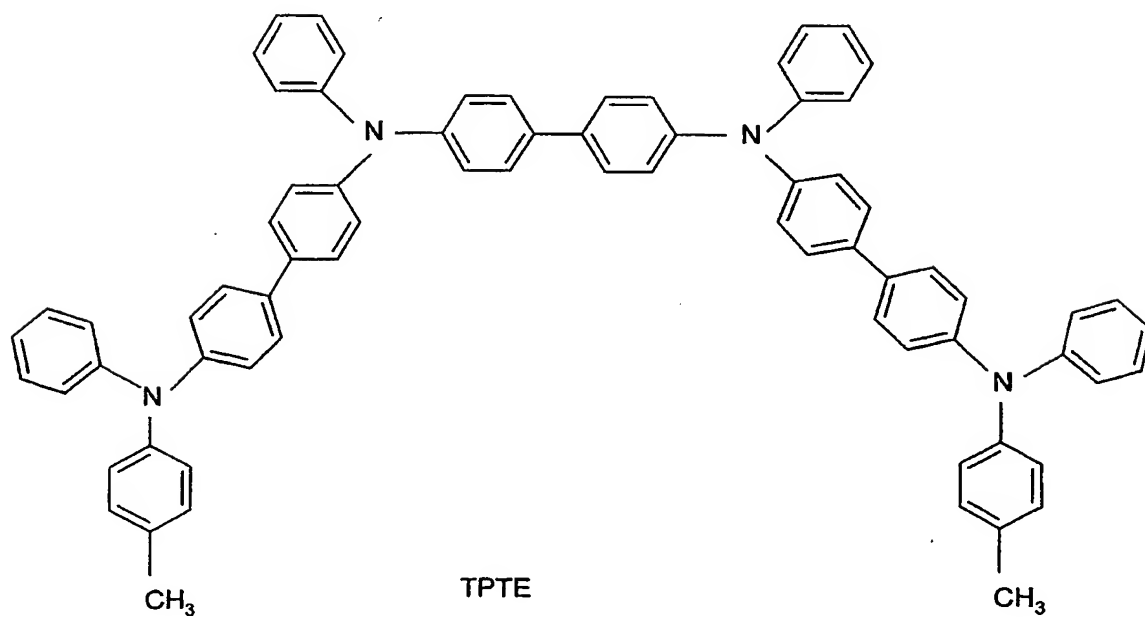


Fig. 15b

16/24

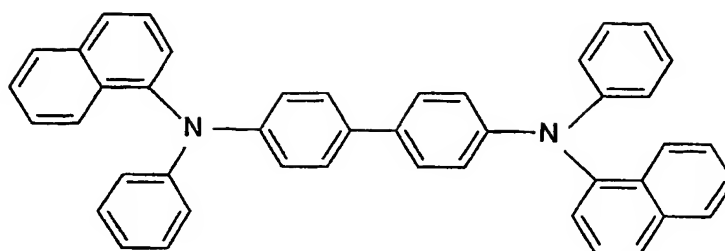
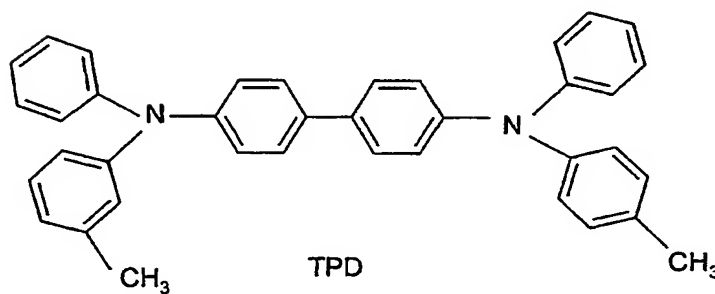
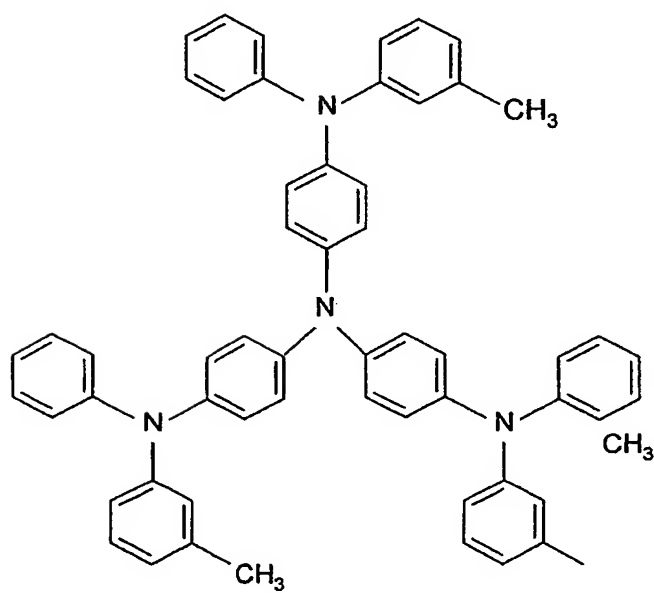
 α -NPB

Fig. 16a



TPD

Fig. 16b



mTADATA

Fig. 16c

17/24

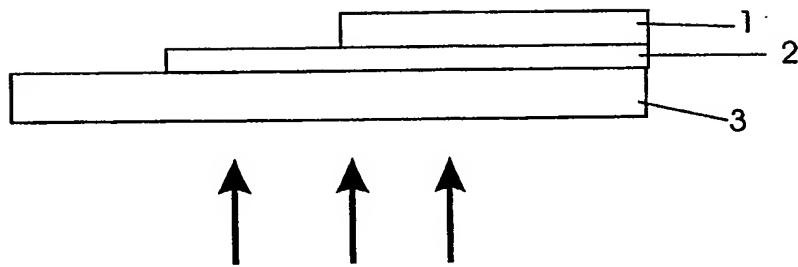


Fig. 17

18/24

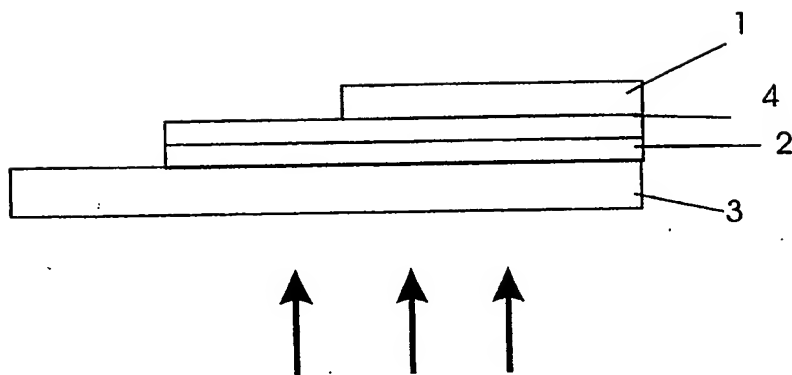


Fig. 18

19/24

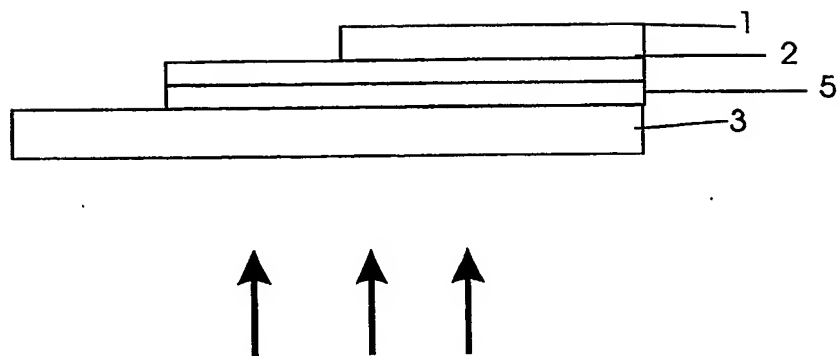


Fig. 19

20/24

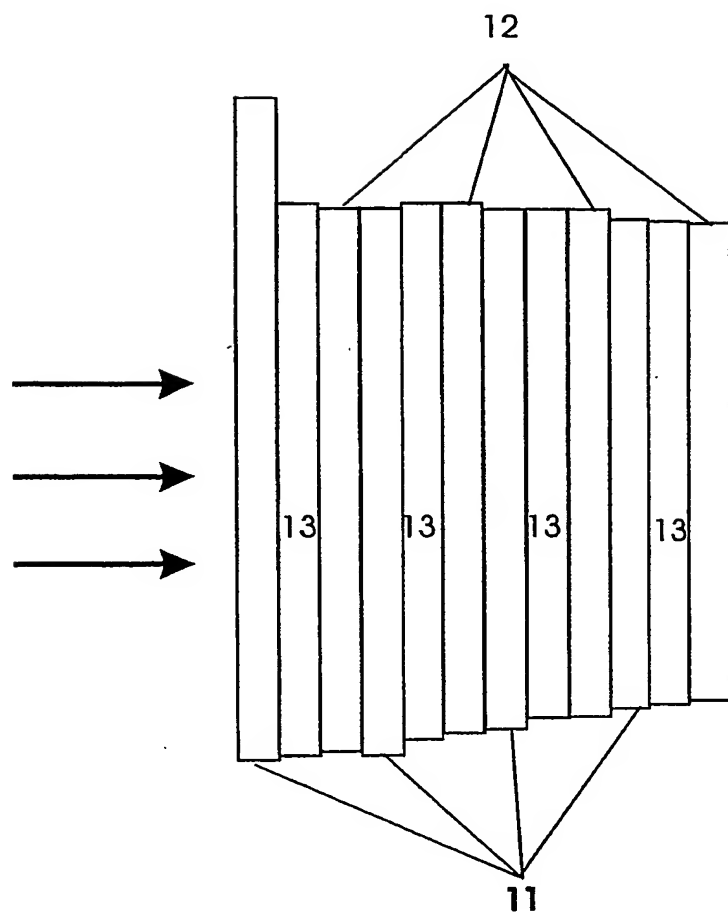


Fig. 20

21/24

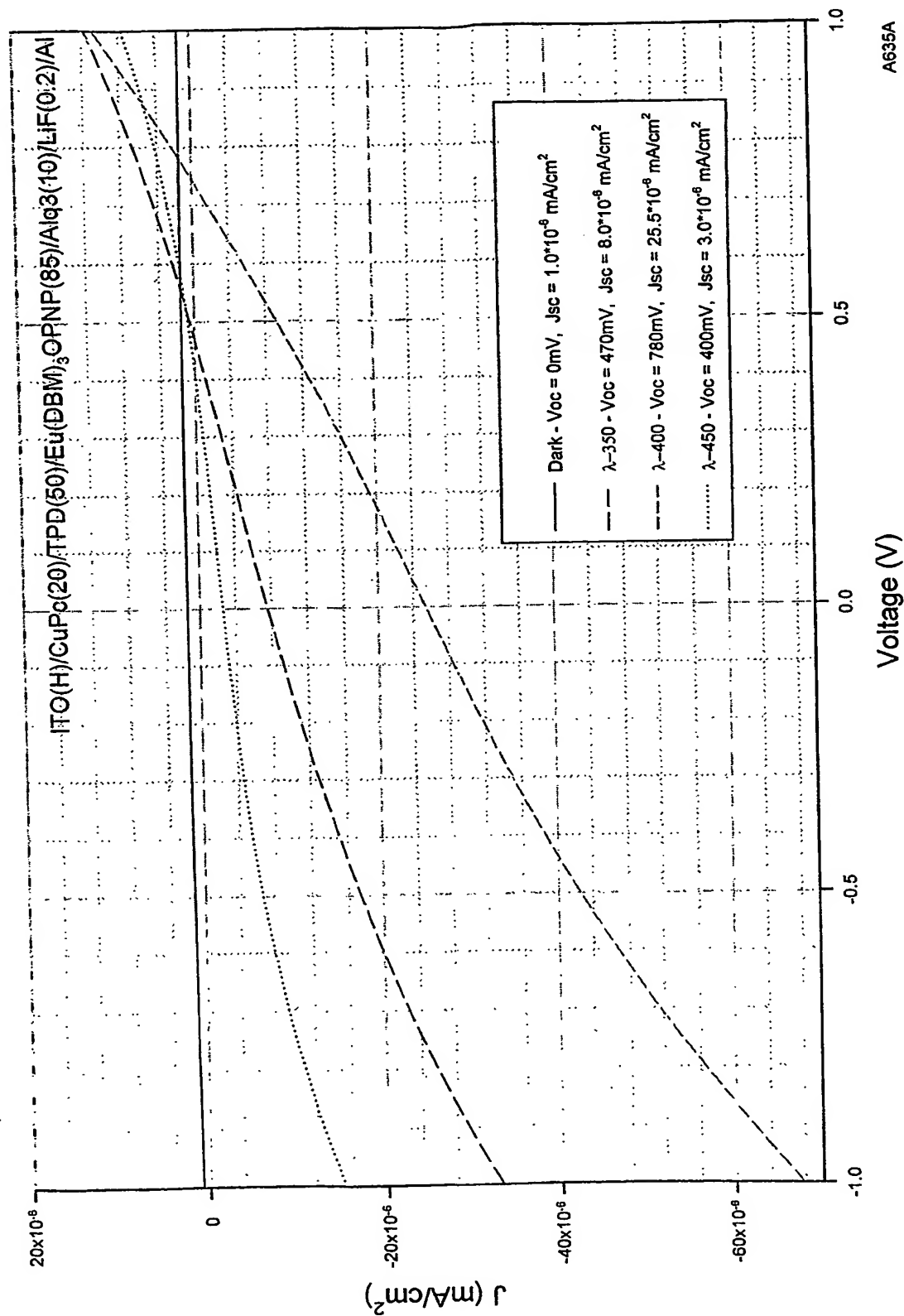
Photovoltaic IV Measurement on $\text{Eu}(\text{DBM})_3$ OPNP

Fig. 21

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22/24

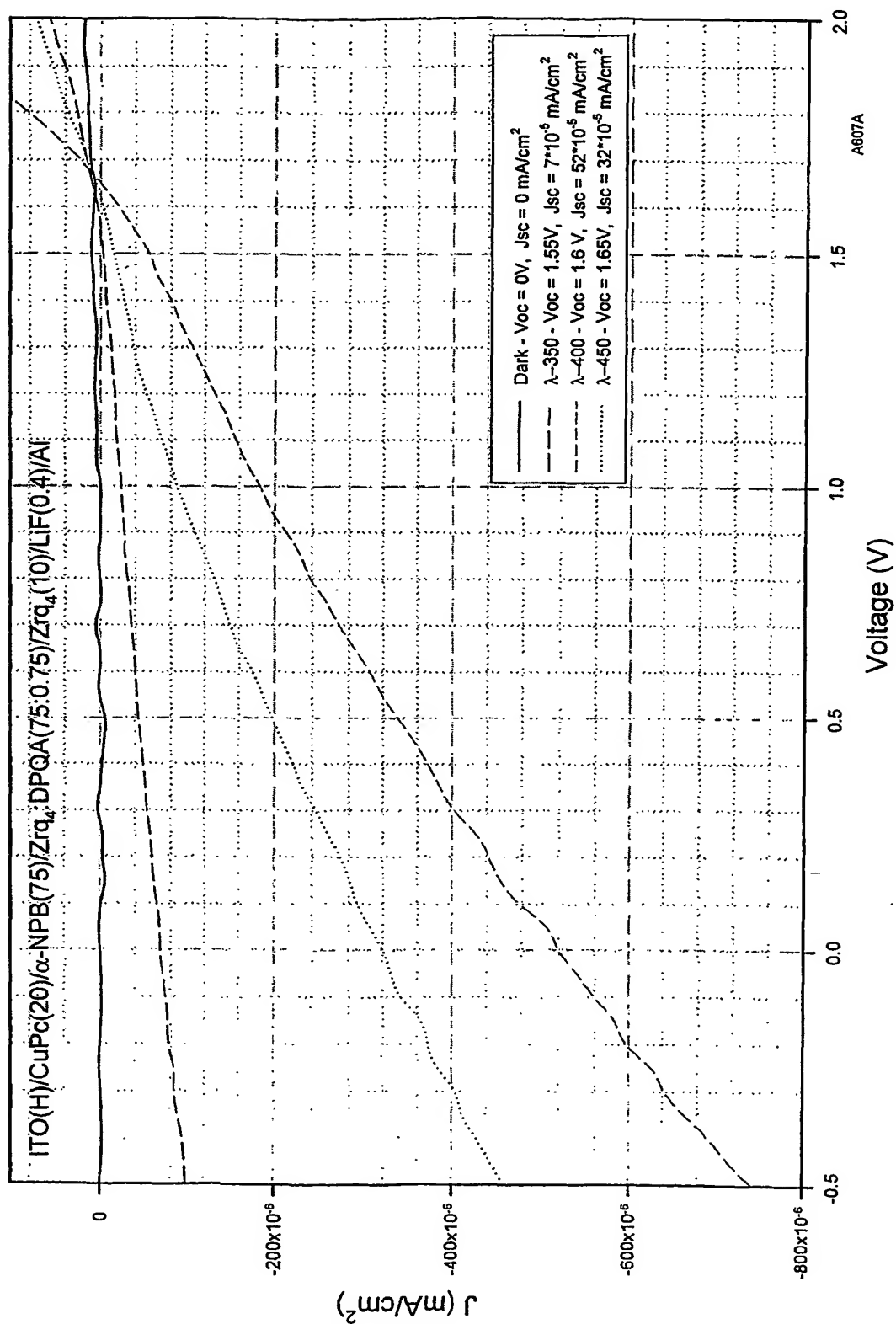
Photovoltaic IV Measurement on ZrQ_4 

Fig. 22

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23/24

Photovoltaic IV Measurement on Liq

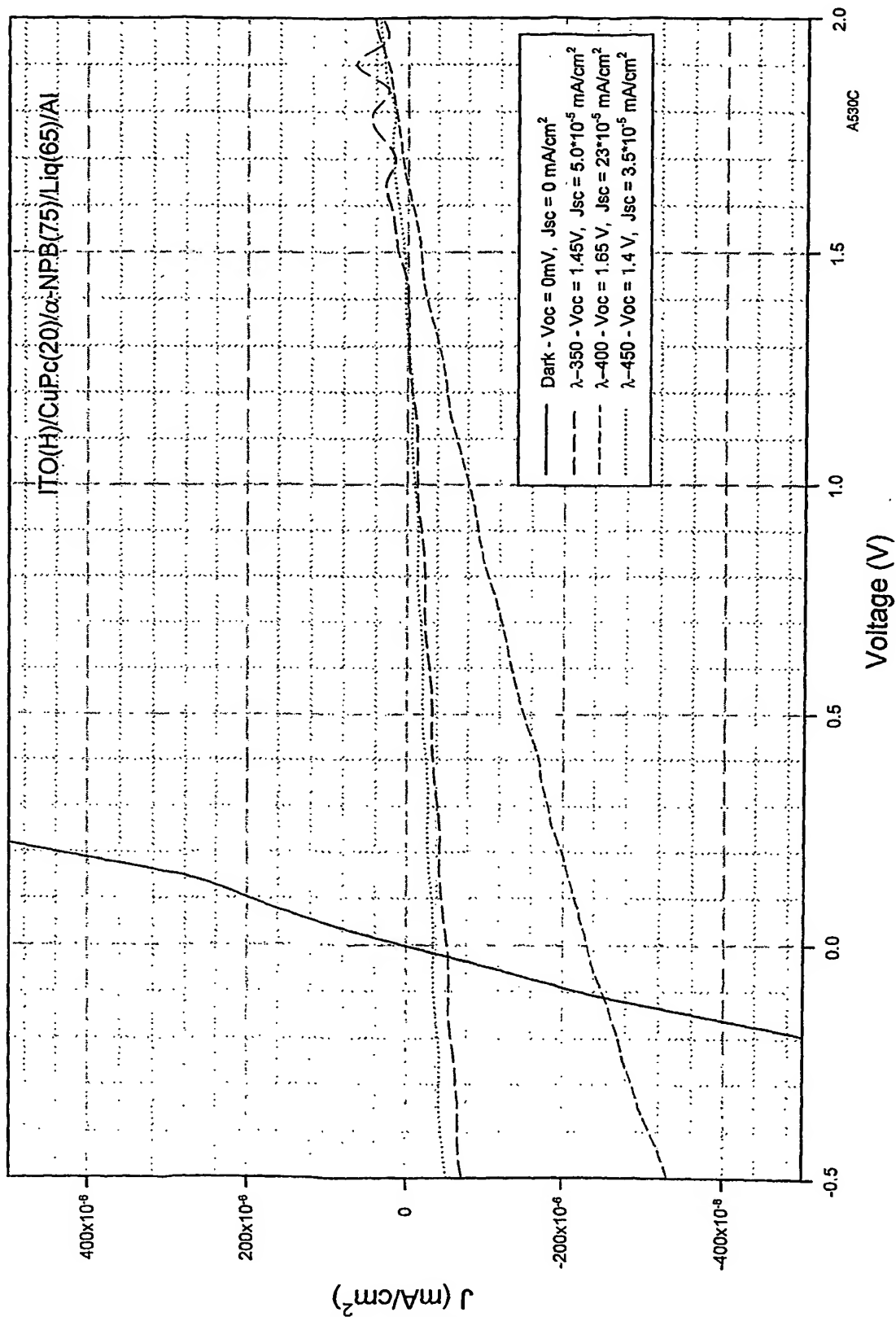


Fig. 23

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24/24

Photovoltaic IV Measurement on Liq

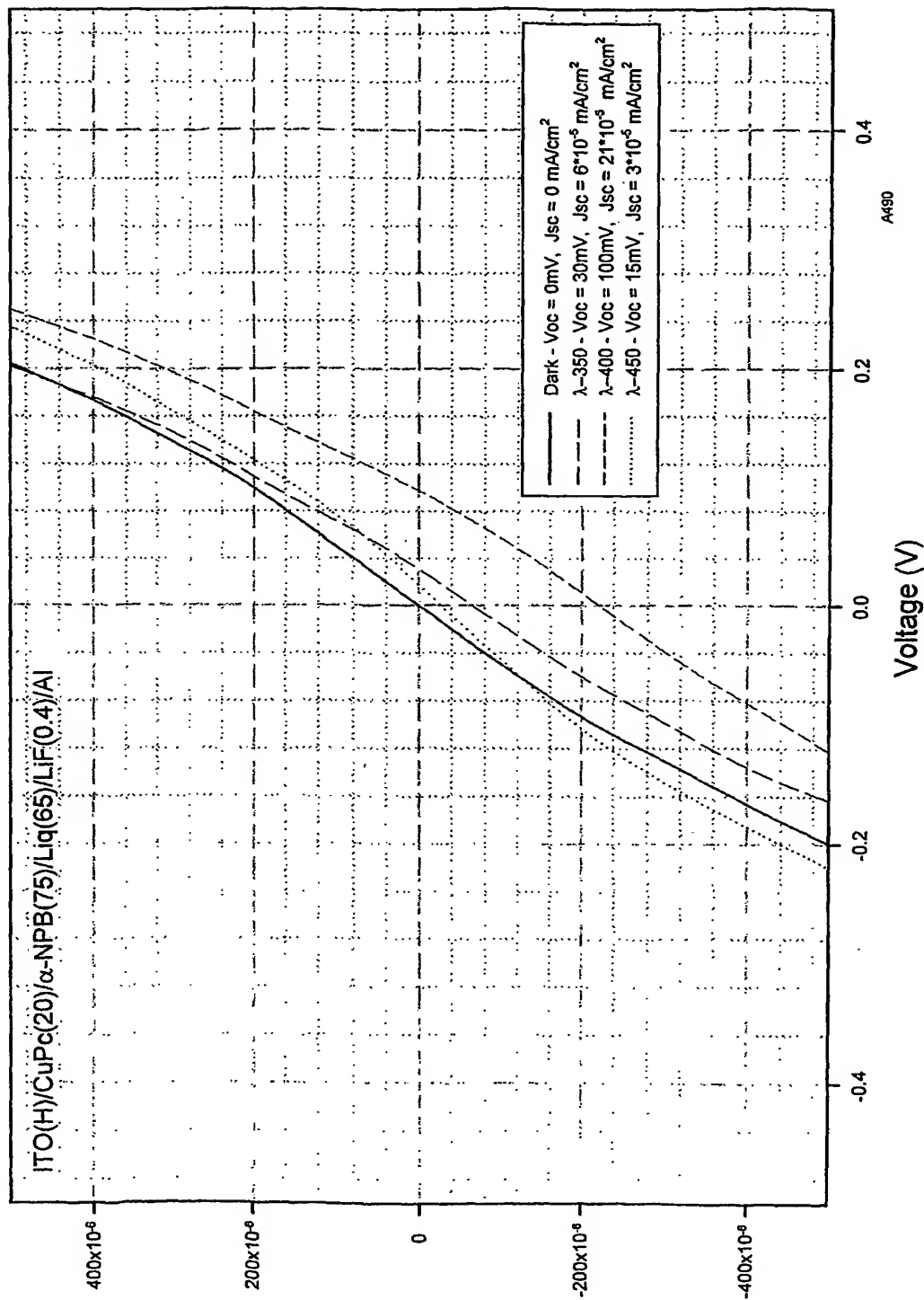


Fig. 24

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	the whole document	9-12
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X	US 6 310 282 B1 (HORIGUCHI AKIHIRO ET AL) 30 October 2001 (2001-10-30) the whole document	1, 12-14
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 September 2004

Date of mailing of the international search report

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Königstein, C

INTERNATIONAL SEARCH REPORT

national Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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INTERNATIONAL SEARCH REPORT

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